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1894

THE RISE AND DEVELOPMENT

OF

ORGANIC CHEMISTRY

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C. Schorlemmer

THE

RISE AND DEVELOPMENT
OF
ORGANIC CHEMISTRY

BY

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PREFACE

THE first edition of this book was published in 1879 and has long been out of print. It was translated into French in 1885 by M. Claparede, and a revised and extended German edition appeared in 1889. Keenly sensible of the value of the work, I frequently urged the author to publish a new edition in English and promised to assist in revising the proofs.

Shortly before the lamented death of Professor Schorlemmer he began to send me the MS. with the request that I would look it through and make any corrections in the language that seemed desirable. At the request of his executors I have now brought the task to completion. While it has been a real pleasure to me to do this, I have found the work longer and more laborious than I anticipated. Professor Schorlemmer told me when he sent the MS., that latterly he had written so much German that he had lost facility in writing English, and I believe indeed that nothing less than re-writing the work would have deprived it of the evidences of its author's nationality. This seemed to me to be unnecessary and even undesirable; for, to his pupils at any rate, I feel sure that the occasional echo of the Author's English will make the work all the more welcome. I have made some corrections and a few additions, but have not altered in any way the plan of the work. I am indebted to my colleague, Dr. Cohen, for valuable help in the revision.

The previous edition of this work was inscribed by Professor Schorlemmer to Hermann Kopp; the present one must go forth as a memorial of its own author—a piece of work eminently characteristic of his genius, disclosing at once the breadth and depth of his knowledge, and his ardent and disinterested love of what he was wont to term, with the pride of a disciple, "our Science."

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BIOGRAPHICAL NOTICE[1]

CARL SCHORLEMMER, the eldest son of Johannes Schorlemmer, was born at Darmstadt on 30th September 1834. He received his early education at the Volksschule, and subsequently at the Realschule of his native town. At this early period his talents and tastes pointed to the adoption of some learned profession, and in spite of the restricted means of his father, Schorlemmer was enabled from the age of sixteen to nineteen to obtain a good grounding in mathematics and natural science at the Darmstadt Gewerbeschule. There he distinguished himself by his intelligence and aptitude, and by the zealous and valuable assistance which he rendered in the Laboratory. Constrained to adopt a calling, he followed the example of his schoolfellow, Dittmar, and in 1852 entered as a

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[1] Several short biographical notices of Professor Schorlemmer have appeared. Sir Henry Roscoe contributed an appreciative sketch to the *Proceedings of the Royal Society* (1892-3, **52**, vii.); Dr. Harden of Owens College wrote a notice for the *Journal of the Chemical Society* (1893, **63**, 761); and Dr. Adolf Spiegel (a former assistant of Professor Schorlemmer) published an account of greater length in the *Berichte* (**25**, 1107 c). I have made free use of these notices.

pupil in an apothecary's shop at Gross-Umstadt where he remained two and a half years. Thence, after passing the Assistants' Examination, he moved to Heidelberg and took a place as apothecary's assistant. At Heidelberg he came under the influence of Bunsen, whose lectures he attended in his spare time; and here also he renewed his intimacy with Dittmar who, having abandoned pharmacy, became, subsequently, Bunsen's assistant.

Inspired with renewed zeal for science by contact with Bunsen, Schorlemmer likewise decided to give up pharmacy, and in May 1859 betook himself to the University of Giessen where, under Will, he received his first systematic instruction in the practical work of scientific chemistry. At Giessen Schorlemmer also attended Hermann Kopp's lectures, and from him doubtless acquired that taste for the historical side of chemistry which he exercised so happily in his writings, and of which the present volume is an outcome.

In August 1859 Schorlemmer once more followed his friend Dittmar, and succeeded him as private assistant to Professor Roscoe at Owens College, Manchester. Here he was exposed to the attractions of applied chemistry, and in a community which had the discernment to employ men like Mond, Caro, Martius, and Pauli, these attractions may have been considerable. Schorlemmer, however, remained steadfast in his academic calling, and in 1861 he received the appointment of Official Assistant in the Owens College Laboratory—again in succession to Dittmar.

In this post he continued until 1874, when in consideration of the eminence he had attained in the scientific world, and at Professor Roscoe's urgent request, he was appointed to a separate chair of Organic Chemistry, a position which he occupied until his death.

Of Schorlemmer's scientific work but modest mention is made in this volume (see p. 141). It was in the year 1861 that he began the researches which led directly to nearly all his subsequent experimental work. Some oils, prepared by the distillation of cannel coal, were sent to the Owens College Laboratory by Mr. John Barrow of Gorton, Manchester. From these Schorlemmer isolated the aliphatic hydrocarbons, fractionated them, and determined their boiling-point, composition, and vapour density. At that time the systematic chemistry of the paraffins had not been worked out, and a large field presented itself for detailed work. But the great interest connected with the study of the paraffins arose from their supposed existence in two distinct isomeric series—one consisting of the alcohol radicals, the other of their hydrides. Ethyl hydride, $C_2H_5 . H$, and methyl, $(CH_3)_2$, were thus supposed to be isomeric. It must be remembered that the conception of the hydrocarbon radicals was arrived at by the consideration of the substitution products obtained from the hydrocarbons, and when, for example, ethyl chloride was converted into ethane by inverse substitution, this hydrocarbon naturally appeared as the hydride of ethyl. Thus, Frankland prepared ethyl hydride by the action of zinc and water on ethyl iodide, and also in conjunction with Kolbe, by the action of potassium on ethyl cyanide in presence of moisture. But it was also thought possible to obtain the free radicals by simple removal of the substituting element or group. By the action of zinc on methyl iodide Frankland had thus prepared "methyl" and ascribed to it the formula CH_3; the same substance had been obtained by Kolbe by the electrolysis of acetic acid. But Gerhardt and Laurent showed that in accordance with Avogadro's rule the formula of methyl must be doubled, and Hofmann likewise pointed out that the physical properties were more in accordance with the doubled formula. They arrived thus at the formula C_2H_6, which was that of ethyl hydride, and they maintained accordingly that the supposed "methyl" was identical with ethyl hydride. It became necessary, therefore, to seek for independent evidence of the supposed isomerism, and Frankland repeated the experiments which he had previously made in conjunction with Kolbe on the chlorination of ethyl hydride, and compared these results with those obtained from a study of the chlorination of the methyl obtained by electrolysis of acetic acid. By the action of two volumes of chlorine on two volumes of each of the gases, two volumes of hydrochloric acid and two volumes of the substitution products were obtained. This spoke for the identity of the two hydrocarbons, but Frankland supposed it possible that in the case of "methyl" only one half of the molecule—or one methyl group, as we should now say—had been attacked, whereas in the ethyl hydride the typical hydrogen atom had been replaced. He accordingly acted on one volume of each hydrocarbon with two volumes of chlorine, and gave as the result that in the case of methyl two volumes of HCl, and one volume of a gas having the formula CH_2Cl were formed; whilst with ethyl hydride two volumes of HCl were produced, together with an oily liquid of the probable formula $C_2H_4Cl_2$. Frankland therefore concluded that methyl and ethyl hydride were essentially different substances, and that the paraffins existed in two isomeric series, the hydrides alone being the true homologues of marsh-gas. He maintained also that there could be no advantage in doubling the formulæ of the free radicals, and that it would indeed be irrational to do so unless the formula of the atom of free hydrogen were also doubled.

It must be borne in mind that the *gravamen* of the evidence adduced by Frankland consisted in the assertion that methyl gave a gaseous chlorine substitution product, whilst ethyl hydride gave a liquid one; the formulæ which were ascribed to these products were more or less arbitrary, and could not help to a decision of the disputed point.

Such was the condition of matters when Schorlemmer began his investigations. The paraffins previously obtained from mineral oil and coal tar by Eisenstuck and by Greville Williams had been regarded as belonging to the free radical series, and a hydrocarbon obtained by Schorlemmer for his cannel oils, and called by him caproyl hydride should therefore have been identical with a hydrocarbon previously obtained by Greville Williams, and called propyl. But Schorlemmer found that, just as Berthelot had obtained methyl chloride and methyl alcohol from methyl hydride so he could obtain a caproyl chloride and caproyl alcohol from his hydrocarbon. He therefore regarded it as a hydride and a true homologue of marsh-gas. This result was confirmed by similar experiments with American petroleum made in the same year by Cahours and Pelouze. To obtain further light upon the subject Schorlemmer next compared the properties of heptyl hydride with ethyl-amyl which, being prepared by the action of sodium on a mixture of ethyl and amyl iodides, was regarded as undoubtedly belonging to the class of free radicals. He found that both hydrocarbons underwent the same reactions and yielded the same products. He also examined the action of chlorine on "amyl," and found that it behaved as decatyl hydride. From these experiments, then, Schorlemmer concluded that among the higher paraffins there was identity and not isomerism between the radicals and the hydrides.

He now proceeded to inquire if this was the case with the lower members of the series, and repeated Frankland's experiments on the action of chlorine on methyl and on ethyl hydride. He took every precaution in the preparation of materials, and in carrying out the details of the work, and found as a result that both hydrocarbons yielded the same products, the chief being ethyl chloride. This result was decisive; the only evidence now remaining to support the view that two isomeric series existed, was to be found in some small differences of boiling-point alleged to exist between certain radicals and their isomeric hydrides. These differences, Schorlemmer observed, arose in all probability from the great difficulty of obtaining the hydrocarbons in a perfectly pure state, and would not be found when due precautions were taken.

The result thus achieved by Schorlemmer was of the utmost importance in the development of organic chemistry.

It is difficult for us now to realise the conditions under which the work was done, or the immediate effect that it produced. We must banish from our minds a fixed belief in the validity of Avogadro's hypothesis and our clear conception of the conditions that determine isomerism; and, in fact, we must shut our eyes to all that has arisen during the last thirty years, to guide us in the exploration of molecular structure, if we are to realise the full merit and consequence of Schorlemmer's discovery. Its most conspicuous effects are to be found in the help it gave to the extension of Kekulé's doctrine of the linking of atoms, and the development of a rational theory of isomerism. It also disclosed the true relation of the hydrocarbons to their substitution products and simplified the chemistry of the whole paraffin group. It is noteworthy that, unlike most of the forward steps in this branch of the science, it was not attended by the immediate production of a legion of new substances. On the contrary, Schorlemmer's work may be said to have annihilated a whole series of hydrocarbons and their derivatives,—a view of the matter which will not fail to secure the grateful recognition of the latter-day student.

The subsequent work of Schorlemmer does not bring us again to so important a crisis, and to refer to this work in detail would be but to quote largely from a systematic treatise on Organic Chemistry. In 1866 he investigated tetramethyl or di-isopropyl, and was led thereby to the discovery of a general method for converting a secondary alcohol into a primary one. He first prepared propane from isopropyl iodide by the action of zinc and hydrochloric acid; the propane so obtained yielded, by the action of chlorine, normal propyl chloride, and from this through the acetate he prepared primary propyl alcohol. He also observed that in the chlorination of propane a certain amount of dichloropropane was formed, and that this, unlike the similarly prepared dichlorethane had the chlorine attached to two different carbon atoms,—a fact established by the preparation from it of propyl glycol.

Schorlemmer devoted much time and labour to the comparison of other synthetically-prepared hydrocarbons with those isolated from petroleum by fractional distillation. The agreement in physical properties was not complete, and was attributed by Schorlemmer to the great number of homologous and isomeric hydrocarbons that are associated in petroleum, and to the practical impossibility of completely separating them. It is not unlikely, as Dr. Spiegel has suggested, that the discrepancy was also partly due to admixture with the unsaturated hydrocarbons which occur abundantly in petroleum.

Schorlemmer showed that the paraffins contained in petroleum were for the most part normal; by the action of chlorine upon the individual hydrocarbon he obtained the primary and secondary alkyl chlorides, and from these the corresponding alcohols which he identified by a study of their oxidation products. By this method he also showed incidentally that the octyl alcohol obtained by the distillation of castor oil was methylhexylcarbinol.

Schorlemmer also made a careful investigation of the relation of the constitution to the boiling-point of the paraffins. He showed that among the lower members of the series of normal paraffins the increment of CH_2 was accompanied by a progressively diminishing increment of the boiling-point until nonane was reached. After this an almost constant increment of 19° for each addition of CH_2 was observed. He showed further that of isomeric paraffins the normal one had the highest boiling-point and the tertiary one the lowest.

In conjunction with Mr. R. S. Dale, Schorlemmer published several papers on Aurin (see p. 108). They made careful analyses of this substance, studied its relations to rosaniline, and obtained from it by distillation with zinc dust, benzene and a hydrocarbon with higher boiling-point. This work might have been attended with very important results had not the researches of E. and O. Fischer on the rosanilines rendered its further prosecution unnecessary, by establishing the fact that aurin was trihydroxy-triphenylcarbinol.

Schorlemmer and Dale also published several papers on suberone. Among the remaining papers published by Schorlemmer, those on the constitution of sulphuric acid and of bleaching powder, in which he advocates the views that are now orthodox, are worth mention if only as indicating the aspect of inorganic chemistry that interested him most. The list of sixty papers which is appended to this notice would in itself bespeak the activity and fruitfulness of Schorlemmer's scientific career; but it is to be remembered that the last fifteen years of his life were continuously and almost exclusively devoted to authorship. He translated Roscoe's *Lessons in Elementary Chemistry* into German in 1867, and in 1874 published as a companion volume his own *Lehrbuch der Kohlenstoffverbindungen.* The English edition of this appeared in 1874 as *A Manual of the Chemistry of the Carbon Compounds or Organic Chemistry.* This at once became a standard work, though like all works on the subject it soon became out of date. Before the time had come for publishing a new edition, the author, in conjunction with Sir Henry Roscoe, had begun upon the great task of writing a *Systematic Treatise on Chemistry.* The first volume of the Treatise was published both in England and Germany in 1877; the first part of volume iii., dealing with organic chemistry, appeared in 1885, and five more parts appeared before the author's death. The book is still incomplete. It is unnecessary to say anything in description of this well-known work. The labour of writing a book of the size on the subject of Organic Chemistry which should be a complete and readable treatise, and not a mere compilation of facts, cannot easily be overestimated.

The first edition of the *Rise and Development of Organic Chemistry* was published in 1879.

Schorlemmer's keen interest in the history of chemistry, in which he had latterly made researches of considerable importance, finally induced him to commence a book upon the whole subject. This unfortunately remained uncompleted at his death, but the portion which he had written, bringing the subject down to the end of last century, will be published shortly.

Schorlemmer's eminence as a chemist was recognised by his admission to the Royal Society in 1871. In 1878 he was elected a member of the American Philosophical Society, and in 1888 the Senate of the University of Glasgow conferred upon him the honorary degree of LL.D.

Of the services rendered to Owens College by Schorlemmer during the thirty-three years of his connection with that institution, it would be difficult to speak too highly. Sir Henry Roscoe, with whose name that of Schorlemmer will ever be associated, has borne ample testimony to the share he had in maintaining the fame of the Owens College Laboratories. Schorlemmer's lectures were an awakening to the genuine student. He spoke from the fulness of his knowledge, and though he had neither the graces of the orator, nor the arts of the populariser, his lectures were admirable in construction and suggestiveness. For many years good notes of his lectures on Chemical Philosophy formed the sole literature available to the student, who desired to learn something of the physical side of chemical science, and to obtain a connected view of chemical doctrine.

As a laboratory teacher Schorlemmer was highly successful, and it was a matter of regret to many that in the latter years of his life the labours of authorship took him so constantly from the laboratory to the study. At the same time there could be no question of the gain to chemical literature. His knowledge of chemistry was that of a laborious student and a clear-sighted philosopher, and his literary presentment of the science was characterised accordingly by a completeness and perspicacity in which he could have been equalled by few, if any, of his contemporaries. He had also a very wide general culture, and his knowledge of botanical science was remarkable.

Schorlemmer had no taste for administrative work, nor for "affairs" of any kind, and he heartily disliked, and as far as possible eschewed, committee work.

To his students Schorlemmer was always accessible, always ready to advise and help; kind, genial, and tolerant. Though of a retiring disposition, he was none the less a delightful companion to his friends; he had the keenest sense of humour, and was an admirable *raconteur.*

Schorlemmer never married, and lived a somewhat solitary life. Though he retained to a remarkable degree the characteristics of his nationality, and an active interest in the political fortunes of Germany (where his sympathies were with the Social Democrats), he fully understood and appreciated the British temperament, and lived contentedly in the country of his adoption. The debt that England owes to him is of the kind that will never loom large in the public eyes, but it is none the less great, and it will be lasting.

The action of the authorities of Owens College in making Schorlemmer Professor of Organic Chemistry, redounded to their credit, and constitutes one of the rare instances of an academic post having been created *ad hominem.* There is no doubt that it added also to the prestige and prosperity of science in the metropolis of industry. Happily the professorship of Organic Chemistry at Owens College has not lapsed with Schorlemmer's death—nor is the fame it acquired in his tenure likely to grow dim.

It is particularly gratifying to think that Schorlemmer's pupils and admirers should have decided to perpetuate his memory by erecting at Owens College a commodious laboratory (now approaching completion) for the prosecution of organic chemistry. This will be the "Schorlemmer Laboratory," and thus most fittingly will the name of Schorlemmer and the traditions of his work pass to posterity.

BIBLIOGRAPHY

THE following is a complete list of the memoirs and notes published by Schorlemmer, amounting in all to sixty distinct papers (*Trans. Chem. Soc.* 1893, **63**, 761):—

1. "On the Hydrides of the Alcohol Radicles existing in the Products of the Destructive Distillation of Cannel Coal." *J. Chem. Soc.* 1862, **15**, 419.

2. "On the Chemical Constitution of American Rock Oil." *Proc. Man. Lit. and Phil. Soc.* **3**, 1862-63, 81.

3. "On the Derivatives of Hydride of Heptyl." *J. Chem. Soc.* 1863, **16**, 216.

4. "On the Chemical Constitution of the so-called Alcohol Radicles." *J. Chem. Soc.* 1863, **16**, 425.

5. "On the Action of Chlorine upon Methyl." *Proc. Roy. Soc.* **13** (1864), 225.

6. "On the Identity of Methyl and Hydride of Ethyl." *J. Chem. Soc.* 1864, **17**, 262.

7-14. "Researches on the Hydrocarbons of the Series C_nH_{2n+2}." *Proc. Roy. Soc.* **14** (1865), 164, 464; **16** (1868), 34, 367, 372; **18** (1870), 25; **19** (1871), 20, 487.

15. "Note on the Hydrocarbons contained in Crude Benzol." *J. Chem. Soc.* 1866, **19**, 356.

16. "Note on Ethyl Hexyl Ether." *J. Chem. Soc.* 1866, **19**, 357.

17. "Note on the Amyl Compounds derived from Petroleum." *Proc. Roy. Soc.* **15** (1867), 131.

18. "On a New Series of Hydrocarbons derived from Coal-tar." *Proc. Roy. Soc.* **15** (1867), 132.

19. "On the Constitution of Capryl Alcohol from Castor-oil." *Proc. Roy. Soc.* **16** (1868), 376.

20-21. "On the Derivatives of Propane (Hydride of Propyl)." *Proc. Roy. Soc.* **17** (1869), 372; **18** (1870), 29.

22. "On the Constitution of Hyposulphurous acid." *J. Chem. Soc.* 1869, **22**, 254.
23. "Formation of Cetyl Alcohol by a singular Reaction." *Proc. Roy. Soc.* **19** (1871), 22.
24. "Berichtigung. Ueber Bleikammerkrystalle." *Ber.* **5** (1872), 378.
25. "On the Boiling-points of the Normal Paraffins and some of their Derivatives." *Proc. Man. Lit. and Phil. Soc.* **11** (1872), 95.
26. "On the Normal Paraffins." *Phil. Trans.* **162** (1872), 111.
27. "On the Heptanes from Petroleum." *J. Chem. Soc.* 1873, **26**, 319.
28. "Ueber die Oenanthylsäure." *Ber.* **6** (1873), 58.
29. "An Improved Method for preparing Marsh Gas." *Proc. Man. Lit. and Phil. Soc.* **13** (1873), 29.
30. "The Chemical Constitution of Bleaching Powder." *Proc. Man. Lit. and Phil. Soc.* **13** (1873), 49.
31. "On the Chemical Constitution of Bleaching Powder." *J. Chem. Soc.* 1874, **27**, 335.
32. "Methylhexylcarbinol." *J. Chem. Soc.* 1874, **27**, 1029.
33. "Note on the Boiling-point of Methylhexylcarbinol." *J. Chem. Soc.* 1875, **28**, 209.
34. "Some Remarks on Mr. T. M. Morgan's Paper." *J. Chem. Soc.* 1875, **28**, 306.
35. "On Groves' Method of Preparing Chlorides." *J. Chem. Soc.* 1875, **28**, 308.
36. "On some Reactions of Bromine and Iodine." *Proc. Man. Lit. and Phil. Soc.* 1875, **4**.
37. "On the Normal Paraffins. Part II." *Phil. Trans.* Part I. 1878, 49.
38. "On the Normal Paraffins. Part III." *Phil. Trans.* Part II. 1880, 451.
39. "On the Origin of the Word Chemistry." *Mem. Man. Lit. and Phil. Soc.* [3], **7**, 75.
40. "The Action of Hydrochloric Acid on Ethylene Alcohol." *Trans. Chem. Soc.* 1881, **39**, 143.
41. "On the Occurrence of Caffeïne in the Leaves of Tea and Coffee grown at Kew Gardens." *Mem. Man. Lit. and Phil. Soc.* [3], **8**, 155.
42. "On the Leaves of *Catha edulis.*" *Mem. Man. Lit. and Phil. Soc.* [3], **8**, 169.
43. "On the Introduction of Coffee into Arabia." *Mem. Man. Lit. and Phil. Soc.* [3], **8**, 215.
44. "Thionyl Chloride." *Proc. Chem. Soc.* 1885, 52.

45. "The History of Creosote, Cedriret and Pittacal." *J. Soc. Chem. Ind.* **4** (1885), 152.
46. "Reduction der Aldehyde zu Alcoholen." *Ann. Chem. Pharm.* **177**, 303.

In conjunction with Grimshaw:—
47. "Oenanthylic Acid and Normal Heptyl Alcohol." *J. Chem. Soc.* 1873, **26**, 1073.
48. "Normal Primary Heptyl Alcohol." *Proc. Roy. Soc.* **21**, 393.

In conjunction with R. S. Dale:—
49-51. "Suberone," *J. Chem. Soc.* 1874, **27**, 935; *Trans.* 1879, **33**, 684; 1881, **39**, 539.
52. "Note on Safranine." *Trans. Chem. Soc.* 1879, **33**, 682.
53. "Suberic and Azelaic Acids." *Trans. Chem. Soc.* 1879, **33**, 683.
54. "On Aurine." *J. Chem. Soc.* 1871, **24**, 466.
55. "On Aurin." *J. Chem. Soc.* 1873, **26**, 434.
56. "Transformation of Aurin into Rosaniline." *J. Chem. Soc.* 1877, **3**, ii. 121.
57. "Ueber die Umwandlung des Aurins in Rosanilin." *Ber.* **10**, 1123.
58. "On Aurin. Part II." *Trans. Chem. Soc.* 1879, **33**, 148.
59. "Transformation of Aurin into Trimethylpararosaniline" (printed by mistake Triphenylpararosaniline). *Trans. Chem. Soc.* 1879, **33**, 562.

In conjunction with T. E. Thorpe:—
60. "On the Normal Paraffins. Part IV." *Phil. Trans.* 1883, Part I. 269.

I

Chemical knowledge of the Ancients—Origin of the word Chemistry—Alchemy—Iatrochemistry—First attempts at a classification—Distinction between inorganic and organic bodies; Lemery—The period of phlogistic chemistry; Becher, Stahl, Scheele—The beginning of quantitative chemistry; Lavoisier, Berzelius, Gmelin—The Aetherin theory.

ORGANIC Chemistry as a science has been developed almost entirely during the present century; it is nevertheless true that facts of universal importance for chemistry were first observed in the case of organic bodies.

The only acid known to the ancients was vinegar or dilute acetic acid; hence its name and the conception of acidity were expressed by closely-related words (*ὄξος*, *acetus*, vinegar; *ὀξύς*, *acidus*, sour). By the action of vinegar on alkalis the first artificial salts were obtained. The first reagent which we find mentioned is an infusion of nut-galls, in which paper was steeped, in order, as Pliny tells us, to ascertain the presence of green vitriol (*atramentum sutorium*) in verdigris. In case of such an adulteration the paper would be blackened by placing the suspected substance on it: "*Deprehenditur et papyro, galla prius macerato; nigrescit enim statim aerugine illita.*" The juice of nut-galls and of the pomegranate was also employed for detecting a kind of alum (*alumen*) used for dyeing wool black; this was either native green vitriol or a mineral containing it.

A crude mode of distillation was also known and used for obtaining oil of turpentine in early times. The Gauls and Germans understood the art of soap-making, and introduced into Rome a process, by the exact study of which, in our days, much light has been thrown on an important part of organic chemistry.

The fermentation of grape-juice was known to prehistoric nations; in Egypt, Gaul, and Germany the art of brewing beer was understood, and in the North mead was made from honey.

The art of dyeing by means of organic substances was highly developed in India, Phœnicia, and Egypt. Besides these, the ancients were acquainted with numerous other organic bodies, such as oils, fats, sugar, starch, gums, resins, indigo, etc., as well as with a number of inorganic substances. Chemistry as a science was, however, unknown to them, the facts being not sufficient to afford a generalisation. It has been stated that those of their philosophers who desired to promote scientific knowledge followed the treacherous path of speculation, instead of the safe way of observation and experiment. This view, which the present writer for some time shared, cannot be maintained, for we find many keen observers among the ancients. Let any one look into Strabo and see what Posidonius says of the tides, or read Heraclitus and he will find evidence of a clearer conception of the inseparable connection between matter and motion than is expressed by many modern physicists.

A new science is not created all at once, springing forth completely armed like Minerva from the head of Jupiter, or in all its beauty like Venus from the foam of the sea. Chemistry as the science of atoms is an offspring of Physics or the science of molecules, and this again is founded on Mechanics or the science of masses. These two sciences had, therefore, to be developed to some extent ere Chemistry, in the crudest shape, could make its appearance.

Chemistry as a science (*scientia chimiae*) is first mentioned by Julius Maternus Firmicus, who in the first half of the fourth century wrote a book on astrology, commonly called Mathesis,[1] founded on older Egyptian writings, and only known in a defective state. He does not inform us what the object of this science was, but it is explained by another writer, living probably at the end of the third century. Zosimus of Panopolis, according to Georgius Syncellus, who wrote in the ninth century, states that χημεία meant the art of making gold and silver, and it is used in the same sense by other Greek writers.[2] Zosimus informs us further, that the precepts for making gold were found cut into stone in the temples of Hephaestus, by which he means the Egyptian god Pthah. In the same place alloys of gold and silver were manufactured, and the doubling or tripling of gold effected.[3]

These old hieroglyphs were afterwards transferred in demotic characters to papyrus, and also translated into Greek.[4] Olympiodorus, another writer of the school of Alexandria, says that these precepts were found in the libraries of Ptolemy.[5]

John of Antioch informs us that in the year 269

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[1] Kopp, *Beiträge Gesch. Chem.* 43.

[2] *Ibid.* 9.

[3] *Collection des anciens Alchimistes Grecs*, par Berthelot et Ruelle, 206.

[4] Berthelot, *Introd. étude de la chimie*, 200.

[5] *Coll.* 95.

a rising of the Egyptians was suppressed by the emperor Diocletian, who, in order to deprive them of further means of resistance, gave the order to burn their book on the chemia of gold and silver.[1] Fragments of these have, however, been preserved in the writings of Pliny and Vitruvius (Berthelot), but chiefly in the Papyrus X, belonging to the collection of antiquities in the University of Leyden, which has been translated by Leemans into Latin,[2] and from this by Berthelot into French.[3] This important document is the oldest chemical manuscript in existence, and consists of 101 precepts, treating chiefly of the working of metals, their purification, the manufacture of alloys, the imitation of the noble metals, and their falsification, the latter being quite openly acknowledged. It is shown how, by means of arsenic or mercury, a white colour is imparted to silver, and by means of cadmia or calamine we may dye copper yellow, or impart to it the colour of gold. Such imitations may be employed for doubling the weight of a given quantity of gold and silver.

From these facts arose the belief, which we first find in the writings of the Greek alchemists belonging to the school of Alexandria, that not only the colour but also other properties of a common metal might be altered in such a way as to convert it into real gold or silver. Now, as the imitation of these was first practised in Egypt, and as Plutarch informs us that this country was formerly called Chemia, which has since been confirmed by hieroglyphics (according to these the old name of Egypt is Chemi), it appears

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[1] Kopp, *loc. cit.* 57 and 83.

[2] *Papyri Graeci musei antiquarii publici Lugduni Batavi* II., 1885.

[3] *Introd.* 19.

most probable that *scientia chemiae* meant originally the *science of Egypt.*[1]

The old Greek alchemists, however, employed it in a different sense. Thus Olympiodorus speaks not only of the *secret art of chemia* (*τὴν κεκρυμμένην τέχνην τῆς χυμείας*), but also of a *chemical book* (*βίβλον χημυτικὴν*); and, as already stated, John of Antioch mentions the books on the *chemia of gold and silver.* Suidas again, who about the year 1000 wrote a lexicon, defines *chemia* as *the making of gold and silver* (*χημεία ἡ τοῦ ἀργύρου καὶ χρυσοῦ κατασκευὴ*). From this it appears that Chemia does not any longer mean the name of a country, but we are not told in what sense the word was then used. This information, however, we find in the writings of the Arabians, who took possession of the inheritance of the Alexandrian alchemists, and translated Chemia into Al-kîmiyâ.

Now Gildemeister has shown that the Arabians did not originally employ this word as an abstraction, but as the name of a substance or the medium by which a transmutation of metals is effected, *i.e.* the philosopher's stone, or, more precisely, a preparation obtained from it.[2]

We may safely assume that the Greek alchemists used the word in the same sense. The name of a country became the name of a substance, a change which is not uncommon, as evident from the use of such words as *Creta* and *Magnesia*, or *Japan.*

But now arises the question, What was this substance? *Chemi* meant not only Egypt, but also *black*, or the *black of the eye*, and we find that as long as the

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[1] Kopp, *loc. cit.* 60; Pott, *Zeitsch. deutsch. morgenländ. Ges.* 30, 6; Berthelot, *Origine Alchim.* 27.

[2] *Zeitsch. deutsch. morgenländ. Ges.* 30, 534.

belief in Alchemy existed, the first steps in the transmutation of the metals was called *blackening* or *melanosis*. We further find that the Greek alchemists used in their operations a most wonderful preparation which they called *ὕδωρ θεῖον*, generally translated *divine water*, but also meaning *sulphurous water*. It appeared impossible to ascertain what was meant by this term until the description of a simple method for preparing the substance was found in the papyrus of Leyden.[1] Berthelot afterwards discovered a still more simple one in the writings of Zosimus, according to whom it is obtained by boiling a mixture of sulphur and quicklime with water. This would produce a solution containing polysulphides of calcium.[2] That such a liquid, which yields with metals or their compounds all possible colorations, and by the addition of vinegar gives a precipitate of finely divided sulphur, at the same time evolving sulphuretted hydrogen, should have excited the fancy of the alchemists will be readily understood.

Zosimus speaks also of the distillation of the divine water, and says all the connections of the apparatus must be well luted in order that the odour be not lost, for though this is very unpleasant, the potency is contained in the odour![3] The preparation must be kept in well-closed vessels and is called divine (*λοιπὸν θεῖον καλεῖται τὸ ὕδωρ τοῦ θείου*) in reference to the vapour which ascends from below to above.[4] When Zosimus quotes from the oracles of Apollo[5]—

> "A blacker, purer, humid vapour,"

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[1] Berthelot, *Introd.* 46.
[2] *Coll.* 202.
[3] *Ibid.* 143.
[4] *Ibid.* 173.
[5] *Ibid.* 152.

he means undoubtedly sulphuretted hydrogen, by means of which *melanosis* was effected; and when Olympiodorus speaks of τέχνη τῆς χημείας, he means probably the preparation of the blackening agent.

Gildemeister has further shown that *kîmiyâ* is synonymous with *iksîr*, which also means the transmuting medium. Alchemy as discipline is called the preparation of *kîmiyâ*, just as it is called the preparation of *iksîr*, or, more shortly, the science of *kîmiyâ*, *i.e.* the substance by which gold and silver are artificially brought to their perfect entity. The Qâmûs or Arabic lexicon gives no other meaning; it explains *aliksîr* by *alkîmiyâ*, and *alkîmiyâ* by *aliksîr*, and these terms indicate any medium which is applied to a metal in order to transport it into the sphere of the sun or the moon; *i.e.* to convert it into gold or silver.

If it is said, "Three cannot be got by three, youth by paint, health by medicaments, wealth by *kîmiyâ*, the parallelism with concretes shows that the word is used here also in the concrete sense. It is the same to-day; the pasha of Nicosia talked with Kotschy much of flowers, chiefly *kimia*, a plant having the property of converting metals into gold."[1]

The later Arabic writers, however, applied the term *alkîmiyâ* to the science. The transition in the meaning of the term is seen in the use of such expressions as "books of *kîmiyâ*," analogous to books of stars and the like. Whilst the word *alkîmiyâ* thus came to denote the science rather than the thing used in the science, the word *aliksîr* was retained as the name of the transmuting medium or the philosopher's stone. *Iksir* is identical with ξήριον, the word used

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[1] Petermann's *Geog. Mittheil.* 8, 294.

by the Alexandrians to denote the stone; and the same word was used by the physicians as the name of a medicine used for the drying of wounds (ξηρός, dry).

If, however, *iksîr* and *kîmiyâ* had originally the same meaning, or at least designated things used for the same purpose, and if the former obtained its name from a characteristic property, one would be led to assume a similar origin for the latter. Now the correlative to dry is moist or liquid, and it was accordingly suggested that the name of our science had been derived from χυμός, liquid, which explains the spelling χυμεία and alchymy, which is of a later date.

Ibn Khaldûn, an eminent Arabian historian, who lived in the fourteenth century, says that the stone, after being treated chemically, yielded a liquid or a powder called *iksîr*, which, when thrown on the molten metals, converted silver into gold, and copper into silver. In opposition to its etymology the word is used here for a liquid, possibly because at that time *kîmiyâ* (originally applied to the liquid transmuting medium) no longer meant the medium, but the science of transmutation. This explains also why, later on in the Western countries, the word elixir came to mean a liquid.[1]

As long as our science existed only as alchemy, the study of inorganic substances naturally made more progress than that of organic bodies. The improved methods of distillation led, however, to the discovery of different essential oils and of alcohol, which was considered as one of the substances from which the philosopher's stone could be prepared. At the same

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[1] *Zeitsch. deutsch. morgenländ. Ges.* 30, 534.

time alcohol was believed to be a most potent medicine, and, therefore, called *aqua vitae.* Raymund Lully, who described several methods of obtaining it as strong as possible, said that it would make old people young again, and was "*consolatio ultima* corporis humani."[1] Lully knew the violent action of nitric acid on spirits of wine, from which it has been inferred that he was acquainted with sweet spirits of nitre. This, however, is not the case, as he allowed the volatile products to escape. He also states that by the dry distillation of tartar an oil may be extracted from it.[2]

Up to the sixteenth century almost the sole object of chemical research had been to find the philosopher's stone. But now chemistry began to develop itself in two new and different paths, opened by two distinguished men—Agricola, the father of Metallurgy, and Paracelsus, the founder of Iatrochemistry or medical chemistry. Both contributed chiefly to the development of inorganic chemistry. It might have been expected that, by the work of the Iatrochemists, the knowledge of organic chemistry would have made great progress. But this was not the case, because, in opposition to the school of Galen and Avicenna, Paracelsus and his followers chiefly employed metallic preparations as medicines. A few, but only a few, of them endeavoured to extract from organic bodies their active medicinal principles. In this way a large number of essential oils were discovered; by the dry distillation of wood *pyroligneous* acid, or *acetum lignorum* was obtained; in the same way impure pyruvic acid, or *spiritus tartari,* was prepared from tartar, and sugar of lead yielded *spiritus ardens e saturno,* or impure acetone.

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[1] Kopp, *Gesch. Chem.* 2, 180.

[2] *Ibid.* 4, 352.

By heating amber, crystals of succinic acid, called *flos* or *sal succini*, were got, and by the same method benzoic acid, or *flores benzoïn*, were extracted from gum benzoin. The action of acids on spirits of wine was also studied, and thus ether, or *oleum vitrioli dulce*, was discovered as well as *spiritus salis dulcis*, an alcoholic solution of ethyl chloride.

A new chapter in the history of chemistry begins with Robert Boyle, who first clearly pointed out that chemistry must be studied for its own sake as a branch of natural science, and as altogether independent of any application for the purposes either of the alchemist or of the physician. It was not to be any longer regarded as the handmaid of any art or profession, but as forming an essential part of the great study of Nature; only thus could it attain to vigorous growth.

Boyle was also the first chemist who clearly grasped the idea of the distinction between elements and compounds. In his *Sceptical Chemist* he upholds the view that it is not possible, as had hitherto been supposed, to state at once the exact number of the ultimate constituents of bodies. He further states that dry distillation does not resolve a substance into its elements, as was then believed, and he proved it by showing that the liquid obtained by the distillation of wood, which was called its volatile or mercurial principle, is not a simple body, but contains, besides pyroligneous acid, an indifferent body, which may be separated by distillation over burnt corals. The crude wood-spirit thus obtained he called *adiaphorous spirit* (*ἀδιάφορος*, indifferent).

Only when the difference between elements and compounds had been clearly recognised, did it become possible to ascertain the composition of bodies by analysis and synthesis, and then only in the case of inorganic substances. At this period we find also, for the first time, a sharp distinction being made between inorganic and organic bodies. Hitherto they had been classified according to their physical properties only, and many terms still in use remind us of that time.

Oil of olives and other fatty oils were classed together with oil of vitriol and oil of tartar (deliquesced potashes); spirit of wine was placed in the same category as stannic chloride (*spiritus fumans Libavii*), ammonia or spirit of hartshorn (*spiritus cornu cervi*), ammonium sulphide (*spiritus fumans Boylei*), hydrochloric acid or spirit of salt (*spiritus salis Glauberanus*), and nitric acid (*spiritus nitri fumans Glauberii*). Chlorides having a soft consistency were called butters, and consequently cow's butter appeared beside zinc chloride (*butyrum zinci*), antimony chloride (*butyrum antimonii*), and arsenic chloride (*butyrum arsenici*). Colourless solids soluble in water, and having a peculiar taste were from Pliny's time called salts, and sugar was therefore included in this class, whilst the coloured salts of the heavy metals were known as vitriols.

In 1675, Nicolas Lemery published his celebrated *Cours de Chymie* which, during the lifetime of the author, went through thirteen editions, and appeared even as late as 1756, naturally in a completely revised form. It was considered as the best text-book, and was translated into Latin, English, German, Italian, and Spanish.

According to Lemery the object of chemistry is to investigate the different substances *qui se rencontrent dans une mixte.* By the last word he understood natural products in general. He divided them into three classes: mineral, vegetable, and animal bodies. To the first belong the metals, minerals, earths, and stones; in the second he classes plants, resins, gums, fungi, fruits, seeds, juices, flowers, mosses, manna, and honey; and the third includes animals, their different parts and their excreta. His classification, being based only on the origin of the different substances, became faulty as he tried to be too consistent. Thus amber and the products of its dry distillation he describes in the mineral part, whilst tartar and other potassium salts are classed among the vegetable substances. Among these also is acetic acid, but the acetates and the products of their dry distillation are treated in the first section. In the third part he speaks only of the distillation of vipers, of the distillation of urine, of wax, and also of honey, which he had already mentioned in the part treating of vegetable substances.

Lemery's classification was soon generally accepted, and the founders of the phlogiston theory endeavoured to develop it, and to justify, from a chemical point of view exclusively, a classification founded only on the origin of chemical substances. Becher had already said in his *Physica subterranea*, 1669, that the elements occurring in the three natural kingdoms were the same, but they were combined in mineral bodies in a more simple manner than in vegetable and animal substances. Stahl, in his *Specimen Becherianum*, 1702, expressed the opinion that in mineral bodies the earthy principle preponderated, whilst vegetable and animal bodies contained more of the aqueous and combustible principles. Both made their appearance when these substances were heated in the absence of air or subjected to dry distillation, water being formed and charcoal left behind.

Stahl's definition of organic chemistry is as admirable as that of chemistry in general: "Chemia, alias Alchymia et Spagirica,[1] est ars corpora vel mixta, vel composita, vel aggregata etiam in principia sua resolvendi, aut ex principiis in talia combinandi."

In the first handbooks of phlogistic chemistry we find the compounds which are now called organic bodies classed among other combustible substances. Sulphur, the different kinds of coal, bitumen, resins, vegetable oils, animal fats, and camphor form a common group. It was supposed that these bodies contained, as proximate constituents, a peculiar oil which was rich in phlogiston.

Neither theoretically nor practically did organic chemistry make much advance up to the end of the phlogistic period. When organic bodies were examined it was for the object of pharmacy or the improvement of technical processes, such as dyeing.

At the end of last century organic chemistry began to make more rapid progress, organic bodies being investigated from a purely scientific point of view. Among the chemists working in this direction Scheele must be mentioned first. He discovered, or first clearly distinguished, the most important organic acids, showing that grapes contained one (tartaric acid) which is quite different from that found in lemons (citric acid); that another (malic acid) existed in apples, and again a new one (oxalic acid) was found in wood-sorrel. The latter he obtained artificially by the

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[1] According to Prantl the origin of this word is based on Plato's view of separating (σπάω) and uniting (ἀγείρω). Libavius, at the beginning of the seventeenth century, gives the same derivation, and says that the word had been recently introduced into the science (Kopp, *Beiträge*, 64).

oxidation of cane-sugar with nitric acid, and found it to be not identical with the one obtained in the same way from milk-sugar. He discovered gallic acid in nut-galls, lactic acid in sour milk, and uric acid in urine.

To prepare some of these acids Scheele devised methods which are still in use. Before his time only succinic and benzoic acids were at all well known, being obtained respectively by means of sublimation from amber and gum benzoin. Scheele showed that benzoic acid forms a lime salt freely soluble in cold water, whereas water dissolves the free acid but sparingly. Benzoic acid could, therefore, be readily obtained by boiling gum benzoin with milk of lime, concentrating the filtrate and separating the acid by means of hydrochloric acid.

On the other hand, he found that malic, tartaric, and citric acids formed insoluble salts with lime or lead oxide, by means of which they might be separated from other substances present in the fruit. By decomposing the salts thus obtained with sulphuric acid, the pure acids were prepared.

Scheele further showed that oils and fats contained a common constituent, the *sweet principle of oils* (Oelsüss) known now as glycerin or glycerol, which, according to him, is related to sugar, not only on account of its taste, but also because both substances yield oxalic acid on being heated with nitric acid.

His friend Bergman worked in a similar direction, whilst Rouelle studied animal chemistry—hitherto quite neglected. Rouelle found in human urine a peculiar crystallisable body, which afterwards was called urea, whilst from the urine of cows and camels he isolated a salt resembling flowers of benzoin (benzoic acid) which afterwards was also found in horses' urine, and for a long time believed to be benzoic acid, until Liebig in 1829 showed that it was a new acid, which he called hippuric acid.

Such researches gave a great impulse to the study of organic bodies, and Lavoisier, after having found the true explanation of the process of combustion, analysed a number of organic compounds. He came to the conclusion that vegetable substances consisted commonly of carbon, hydrogen, and oxygen, whilst those formed in the animal organism usually contained, besides these elements, nitrogen and sometimes phosphorus.

Lavoisier's chemistry was essentially the chemistry of oxygen and its compounds; consequently, on examining a body, he endeavoured to find out whether it could be combined with oxygen or already contained it. That portion of a compound which is combined with oxygen he called "*la base*" or "*le radical.*" These terms were first employed by his friend Guyton de Morveau, who, after speaking of the acids of nitrogen, carbon, sulphur, and phosphorus, goes on to discuss the nomenclature of the acids of unknown composition, such as muriatic acid, boracic acid, and acetic acid, etc. With regard to them he says: "Nous nous sommes contenté de désigner l'être simple qui y modifie l'oxygène par l'expression de BASE ACIDIFIABLE, ou, pour abréger, de RADICAL de tel acide; afin de garder la même analogie, et de pouvoir considérer à leur tour chacun de ces êtres d'une manière abstraite."[1]

Lavoisier extended these views; a radical could be a simple or compound body, and thus he says: "Le carbone est le radical de l'acide carbonique;" while

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[1] *Mémoire sur le Développement des Principes méthodique,* 1787.

vegetable acids contain "le radical oxalique, tartarique," etc.

The difference between inorganic and organic compounds he defines as follows:[1]

"J'ai déjà fait observer, que dans le règne minéral, presque tous les radicaux oxidables et acidifiables étaient simples; que dans le règne végétal, au contraire, et surtout dans le règne animal, il n'en existait pas qui ne fussent composés au moins de deux substances, d'hydrogène et de carbone; que souvent l'azote et le phosphore s'y réunissaient, et qu'il en résultait des radicaux à quatre bases."

Lavoisier observed that an element could form more than one oxide; and from this he concluded that organic radicals behaved in the same way; he therefore considered sugar as the neutral oxide "d'un radical hydro-carboneux," and oxalic acid as its higher oxide. He went even so far as to suggest that the fatty oils, which he believed to be hydrocarbons, might actually constitute organic radicals in the free state, and might, by oxidation, be converted into neutral oxides and vegetable acids.

Of Lavoisier's other researches in the field of organic chemistry, his investigation of the process of vinous fermentation must be mentioned, not so much because he first proved that sugar is thus resolved into alcohol and carbon dioxide, as because he clearly understood the importance of this observation. He showed that such a chemical change can be expressed by an equation which may be controlled by analysis, inasmuch as the weight of the original substance, as well as each of the elements contained in it, must be found again in the products.

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[1] *Traité élémentaire de Chimie*, 1793, i. 209.

Lavoisier, however, did not consider organic chemistry as a separate part of the science; and still less did he define it as the chemistry of compound radicals, as has been sometimes stated. He placed all acids together and subdivided them, like Lemery, into mineral, vegetable, and animal acids. His immediate followers, with a few exceptions, did the same. In Gren's *Natural Philosophy*, published at the end of last century, we find the organic compounds treated in a separate chapter; they are defined as the proximate constituents of the vegetable and animal organism, composed only of a limited number of elements in manifold proportions, and not capable of being produced artificially. When, however, it was found that several compounds occur both in the vegetable and animal kingdom, and consequently that no difference between vegetable and animal chemistry existed, the division into inorganic and organic chemistry was generally adopted.

For a long time subsequently uncertainty and difference of opinion prevailed as to the boundary of the two. One reason was that mineral bodies, as well as a few which had to be regarded as organic, gave on analysis numbers showing clearly that their composition was in accordance with the laws of constant and multiple proportions. The majority of organic compounds, however, appeared, as Berzelius said in 1811, not to obey these laws. He proposed, therefore, to decide this question by the analysis of a large number of them, and for this purpose improved the methods of organic analysis. The results obtained proved that although most organic compounds had a much more complicated composition than the inorganic, yet they followed the above-named laws.

Adopting the views of Lavoisier, Berzelius says: "After we have got a clearer insight into the difference existing between the products of organic and inorganic nature, and the different manner in which their ultimate components are united with each other, we find this difference consists really in the fact that in inorganic nature all oxidised bodies contain a *simple radical,* while all organic substances are *oxides of compound radicals.* The radicals of vegetable substances consist generally of carbon and hydrogen, and those of animal substances of carbon, hydrogen, and nitrogen."[1]

Berzelius did not develop these views at once, nor did he enter on any discussion of these hypothetical radicals, although an excellent example of a compound radical had become known by Gay-Lussac's discovery of cyanogen in 1815. Its compounds, however, were at that time believed by most chemists to belong to inorganic chemistry.

Thus a boundary line was still wanting. L. Gmelin, in 1817, said in his handbook of theoretical chemistry, that although inorganic and organic compounds must be kept strictly separate, the difference between them could be more easily felt than defined. As characteristic for the former he fixed upon their binary constitution, the most simple consisting only of two elements, such as the basic and acid oxides, which by combining form a binary compound of a higher order or a salt. The most simple organic compounds, on the other hand, had a ternary constitution or were composed of three elements; moreover, their elements were not combined in such simple proportions of their atomic weights as was the case with inorganic bodies. Consequently Gmelin describes marsh gas, olefiant gas,

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[1] *Lehrb. Chem.* 1817, 1, 544.

cyanogen, etc., in the inorganic part of his book. A marked difference between inorganic and organic compounds he finds also in the fact that the former can be built up artificially from their elements, but not so the latter.

Another view held at that time had, in some respects, a resemblance to that of Stahl, according to which organic bodies consisted of an aqueous and a combustible principle. Lavoisier himself, in the account of his researches on fermentation, stated that it was only with difficulty he got rid of this conception, and could regard sugar, not as a compound of carbon with water, but of carbon with hydrogen and oxygen.

Gay-Lussac found, in 1815, that the vapour-density of alcohol was equal to the sum of the vapour-densities of water and olefiant gas, and that the vapour-density of ether was equal to that of water plus twice that of olefiant gas. In the next year Robiquet and Colin showed that hydrochloric ether could be regarded as a compound of hydrochloric acid and olefiant gas.

Starting with these observations, Dumas and Boullay brought forward a theory according to which alcohol and many of its derivatives could be viewed as compounds containing olefiant gas (*hydrogène bicarboné*) as a proximate component, and might be compared with the compounds of ammonia. The following table is taken from their memoir,[1] the formulæ being, however, expressed by our present notation :—

Hydro-chlorate d'hydrogène bicarboné (éther hydrochlorique),	Hydro-chlorate d'ammoniaque,
C_2H_4, HCl	NH_3, HCl

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[1] *Ann. chim. phys.* 37, 15.

Hypo-nitrite d'hydrogène bicarboné hydraté (éther nitrique), C_2H_4, HNO_2	Hypo-nitrite d'ammoniaque hydraté, NH_3, HNO_2
Bisulfate d'hydrogène bicarboné (acide sulfovinique), C_2H_4, H_2SO_4	Bisulfate d'ammoniaque, NH_3, H_2SO_4
Hydrate d'hydrogène bicarboné (alcool), C_2H_4, H_2O	Ammoniaque liquide, NH_3, H_2O
Hydrate d'hydrogène bicarboné bibasique (éther sulfurique), $(C_2H_4)_2H_2O$.	— — — —

These views were extended not only to other derivatives of alcohol, but to compounds such as the sugars, which were compared with the carbonates of ammonia.

Berzelius at first opposed this theory, but afterwards accepted it, and proposed for olefiant gas the name *Aetherin.*[1] Although we find here for the first time a large number of organic compounds considered from a single point of view, the aetherin theory was not generally accepted as it was not possible to extend it to a larger number of compounds. It was in opposition, too, to several facts. Thus olefiant gas and ether could be obtained by taking water out of alcohol; but neither could these compounds nor others of the group be prepared from their supposed components, as was the case with the ammonia compounds.

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[1] *Pogg. Ann.* 3, 286.

II

The belief in a so-called vital force—The first artificial production of an organic compound—Organic radicals—The Theory of Substitution ; Dumas, Laurent ; Berzelius' opposition—The Nucleus Theory.

AT the period we have now reached we find Berzelius laying stress again on a difference between organic and inorganic substances, first pointed out by Gmelin, and according to which the latter but not the former could be prepared artificially.[1] Berzelius was of opinion that within the sphere of living nature, the elements obeyed laws totally different from those ruling in inanimate nature. It was then commonly supposed that the compounds found in plants and animals were produced by the action of a so-called vital force; and that, although they might be changed into other compounds, none of them could be prepared artificially from their elements. Thus grape-sugar, a compound widely distributed in the vegetable kingdom, by fermentation yielded alcohol, which could be converted into ether, acetic acid, and many other compounds; and all these were considered to be organic, as none of them could be prepared synthetically.

In the year 1828 Wöhler made the important discovery that cyanate of ammonia, which was regarded

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[1] *Lehrb.* 1827.

as an inorganic compound, could be converted quite readily into urea, a body hitherto only known as a product of animal metabolism. Wöhler communicated this discovery to Berzelius in the following words: "I must tell you that I can prepare urea without requiring a kidney or an animal, either man or dog." A comparative investigation of natural urea and cyanogen-urea had proved their complete identity, and established the fact that urine-urea had the same composition as cyanate of ammonia.

But this, the first synthesis of an organic compound, remained incomplete for the time being; and Wöhler understood this, for he says at the end of his letter: "This artificial formation of urea,—can it be regarded as an example of the formation of an organic substance from inorganic matter? It is remarkable that in order to produce cyanic acid (and ammonia too) we must start with an organic substance, and a 'Naturphilosoph' would say that animal charcoal, as well as the cyanogen compounds prepared from it, still retained something of an organic nature, and therefore it might be possible to produce out of them some other organic body."[1]

This synthesis, moreover, remained an isolated fact for a long time, and did not shake the belief in a mysterious vital force. It was maintained that urea, being an excretion of the animal body, and easily resolvable into ammonia and carbon dioxide, might be looked upon as a connecting link between organic and inorganic compounds; that such bodies standing on the boundary line might be prepared artificially, but not those having a less simple constitution.

The belief in such a vital force has long since

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[1] *Bruchstücke aus den Briefen Wöhlers an Berzelius*, 42.

disappeared; to-day we know that the same chemical laws rule animate and inanimate nature. As soon as the constitution of a compound produced in the organic world has been cleared up, we are able to produce it artificially in the laboratory.

In 1832 Wöhler and Liebig published their classical investigation *Researches on the Radical of Benzoic Acid,* in which they showed that oil of bitter almonds, benzoic acid, and a number of compounds obtained from them, group themselves round a "compound element," which they called Benzoyl, C_7H_5O (the ending from ὕλη, stuff or matter). They communicated their results to Berzelius, who in his reply said: "The results you have drawn from the investigation of oil of bitter almonds are certainly the most important hitherto attained in vegetable chemistry; they promise to shed an unexpected light on this part of our science.

"That a body consisting of carbon, hydrogen, and oxygen, combines with other bodies, in particular with those forming salts or bases, and combines with them in the same way as a simple body would—this circumstance proves that there exist atoms (of the first order) having a ternary composition. The radical of benzoic acid is the first and fully proved example of a ternary body possessing the properties of a simple one.

"The facts ascertained by you give rise to such considerations that they may well be regarded as the beginning of a new day in vegetable chemistry. I would therefore propose to call the first discovered radical, consisting of more than two bodies, *Proïn* (from πρωῒ, 'beginning of the day,' in the sense of ἀπὸ πρωῒ ἕως ἑσπέρας, Acts xxviii. 23) or *Orthrin* (from ὀρθρός, dawn of the morning)."

As, however, the long-adopted name benzoic acid would have had to be changed, and as we are accustomed to respect terms so long in general use as not involving any ambiguity, it appeared best to accept the word *Benzoyl.*[1]

What a degree of excitement in the chemical world was created by this research is well seen from the following extract from a letter which Pelouze addressed to Liebig: "On ne parle pas plus à Paris dans le monde chimique que de vos experiences. Venez donc avec M. Wöhler, venez y recevoir le tribut d'hommages qui vous est dû."

To appreciate the effect of this discovery of Wöhler and Liebig's we must recall to mind the unique position which at that period was assigned to oxygen. It was the element which by union with the metals produced bases and with the non-metal acids, and, generally speaking, it was regarded as an element which conferred a distinctive property on its compounds. It was this dominance of oxygen in inorganic chemistry which naturally led Berzelius, as we have seen, to regard many organic substances as the oxides of certain organic radicals. When, therefore, it was established that an organic *radical* like benzoyl already *contained* oxygen the dominance of this element could no longer be maintained so far as organic chemistry was concerned. It is difficult for us now to imagine the revolution which was produced by the mere relegation of oxygen, which had been supreme since Lavoisier's days, to the rank and file of the other chemical elements.

After the discovery of benzoyl, the theory of compound radicals was further developed by Berzelius and

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[1] *Ann. Chem. Pharm.* 3, 282.

Liebig. Although both opposed the aetherin theory, according to which alcohol and ether were compounds of olefiant gas with water, or hydrates of this hydrocarbon, their views did not always agree.

Berzelius regarded alcohol and ether as oxides of two different radicals, whilst Liebig, in a memoir which forms the corner-stone of the radical theory, showed that both contain the same radical which he called *Ethyl*, ether being its oxide and alcohol a hydrate of the latter.[1] The bodies produced by the action of hydrochloric acid, hydriodic acid, sulphuric acid, etc., on alcohol, were, according to Liebig, saline compounds of ethyl oxide, which might be compared with those obtained from potash. In the same way he explained the constitution of other alcohols and their derivatives; and he went even so far as to predict the possible isolation of the alcohol radicals, which perhaps might be effected by the action of potassium on the chlorides or iodides.

By oxidation the alcohols are converted into monobasic acids; methyl alcohol or wood-spirit, CH_4O, yielding formic acid, CH_2O_2, and ethyl alcohol or spirits of wine, C_2H_6O, being converted into acetic acid, $C_2H_4O_2$, bodies whose properties resemble those of benzoic acid.

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[1] *Ann. Chem. Pharm.* 9, 1. Dr. Robert Kane, in a paper published as early as 1833, stated that just as the ammonium theory of Berzelius assumes that the addition of one atom of hydrogen to ammonia converts it into a body resembling in many respects the metals, so we might assume the compounds of aetherin to contain a group consisting of olefiant gas (or an isomeric body) plus one atom of hydrogen. This group he called *Aethereum* (Dublin, *Journ. Med. Chem. Science*, 2, 348). This paper hardly became known beyond Dublin, and Kane says himself, that his speculations were a subject of amusement and ridicule among the chemical circles of that city (*Phil. Mag.* 14, 163). Liebig was certainly not influenced by it, and it was only after the views of the latter were generally accepted that Kane brought forward his claims.

From this it was concluded that they contained the radicals CHO, C_2H_3O.

Berzelius opposed this view. In 1833 he had observed that benzoyl, C_7H_5O, although behaving in many respects like a simple body, must be regarded as the oxide of a hydrocarbon-radical, which he called *Picramyl*, C_7H_5 (πικρός, bitter; ἀμυγδάλη, almond), and that like other oxides it could combine with more oxygen to form an acid. Thus the true radical of formic acid would be *formyl*, CH, and that of acetic acid, *acetyl*, C_2H_3. Liebig agreed to this view, because it allowed the grouping of a certain number of compounds round a common centre. Regnault, for instance, had found in 1835 that Dutch liquid, $C_2H_4Cl_2$, by the action of alcoholic potash is converted into the compound C_2H_3Cl, and Liebig about the same time had discovered aldehyde, C_2H_4O, which is easily oxidised to acetic acid. Regnault's compound was consequently regarded as acetyl chloride, and aldehyde and acetic acid as the hydrates of two different oxides of acetyl.

Chloroform, $CHCl_3$, another of Liebig's discoveries, appeared now as formyl trichloride; being converted by the action of alkalis into formic acid it seemed to stand in the same relation to the latter, as phosphorous trichloride to phosphorous acid.[1]

Dumas, who had an interview with Liebig in 1837, accepted these views, and in a paper published in Liebig's and his own name, he said that nature formed from a small number of elements the large host of

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[1] At that time the equivalent weights were generally used ($C=6$; $O=8$; $H=1$) and the following formulæ employed: water, HO; ether, C_4H_5O; alcohol, C_4H_5O, HO; aldehyde, C_4H_3O, HO; acetic acid, $C_4H_3O_3$, HO; chloroform, C_2HCl_3; formic acid, C_2HO_3, HO, etc.

organic compounds, by first forming radicals, some of which behave like chlorine or oxygen and some like metals. Such radicals as cyanogen, ethyl, benzoyl he looked upon as the true elements of organic chemistry, and not the simple bodies, carbon, hydrogen, etc., which made their appearance only after the organic compounds had been completely broken up. Liebig and he, in conjunction with younger chemists, had set themselves the task of discovering other radicals, which, like those mentioned above, should be composed of a few elements only, and in which they believed the whole secret of organic chemistry to be contained. Liebig and Dumas had been requested by the British Association to prepare for its next meeting a report on the existing state of organic chemistry. The co-operation of the English chemists had been promised; Liebig's name was a guarantee for that of the North European chemists; and Dumas himself promised the support of the French.[1]

The new day in organic chemistry, predicted by Berzelius, so far seemed to advance peacefully; yet threatening clouds had already appeared on the horizon, and a violent storm soon broke out.

While Berzelius and Liebig remained faithful to their theories, and the latter defined organic chemistry as the *chemistry of compound radicals*,[2] Dumas had arrived at conceptions which appeared incompatible with the theory of compound radicals. That theory in its fundamental principles was electro-chemical and dualistic like that which dominated the inorganic chemistry of the time, the only difference being that in the former the radicals played the same part as the elements in the latter.

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[1] *Compt. rend.* 5, 567.

[2] *Handb. Org. Chem.* 1843, 1.

Liebig, in discussing this question in 1838, said: "In the history of the evolution of any science, the researches of a given period of time furnish certain general relations, which every moment are changed and improved upon by new discoveries. Thus an endeavour arises to arrange the newly-discovered facts and to find the common bond by which they are linked together.

"The foundation of every view on the constitution of a compound lies evidently in a positive knowledge of the proportions by weight in which the elements are united with each other; we must know first of all how much of each of these elements a body contains. The variation in the composition of two or more bodies of different properties is in many cases so small and the errors of our analytical methods so large that analysis leaves us in the dark as to the number of atoms of each element. For this reason a perfectly new method of investigation had to be created, which in inorganic chemistry is rarely employed; we are obliged to combine the body with another of known composition, or to resolve it into two, three, or more products, and if the quantity and composition of these products bear a direct relation to the quantity and the composition of the substance from which they have been obtained, any doubts as to the true composition of the latter come to an end. We follow therefore the method of the mathematician and try to determine or to represent an unknown quantity by equations.

"The equations thus obtained give, in a few cases only, a clue as to the mode in which the elements are combined with each other; but we have, in the behaviour of inorganic compounds, distinct and unerring rules for conclusions of this kind. By submitting the body to certain changes similar to those which an inorganic body of an analogous kind undergoes under the same conditions, we conclude from a similar behaviour that its constitution is similar, or *vice versâ*. We therefore compare the combinations formed by an organic body, whenever they possess properties similar to those of a known substance, with the composition and the deportment of the latter. Thus we have been led to the conception of certain combinations, which remain unchanged through a series of chemical changes, of compound bodies which may be replaced by elements, and in whose combinations with a simple body the latter may be replaced by another simple body; bodies consequently which in their compounds take the place of simple bodies, and in fact play the part of elements. Thus has arisen the conception of compound radicals.

"We therefore call cyanogen a radical[1] because it is the never-varying constituent of a series of compounds; because it can be replaced in these by simple bodies; because in its combinations with a simple body, the latter can be separated and replaced by equivalents of other simple bodies.

"Of these three chief characteristics of a compound radical, two at least must be fulfilled, ere it can really be regarded as a compound radical."[1]

Liebig's definition of a compound radical holds good to this day.

According to the radical theory, radicals were divided, like the elements, into electro-positive, forming bases, and electro-negative, forming acid oxides. To the former belonged the metals, hydrogen, and the alcohol radicals, while the latter included the elements

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[1] *Ann. Chem. Pharm.* 25, 1.

of the chlorine group, cyanogen, benzoyl, and other acid radicals.

Gradually, however, facts became known, which could not be brought into accord with this theory. On examining the action of chlorine on organic bodies and on compounds believed to be nearly related to them, it was found that hydrogen was removed and replaced by chlorine.

As early as 1815 Gay-Lussac had observed that by treating prussic acid, CNH (*acide hydrocyanique*), with this element it is converted into cyanogen chloride, CNCl (*acide chlorcyanique*), chlorine replacing hydrogen completely. Some time afterwards he found that when beeswax was bleached by means of chlorine, it lost hydrogen and took up an equal volume of chlorine.[1] Faraday showed, in 1821, that Dutch liquid, $C_2H_4Cl_2$ (ethylene dichloride), was converted by the continued action of chlorine into carbon sesquichloride, C_2Cl_6, and he pointed out that in this case hydrogen was replaced, volume for volume, by chlorine. In their research on the benzoyl compounds (1832), Wöhler and Liebig found that chlorine converted oil of bitter almonds or benzoyl hydride, C_7H_6O, into benzoyl chloride, C_7H_5ClO, which, according to their view, was produced by chlorine taking the place of one atom of hydrogen, this being given off as hydrochloric acid.

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Hardly any notice was taken of these isolated facts before 1834, when Dumas called attention to them, the occasion being, according to Hofmann, a soiree at the Tuileries, when the candles burnt with a smoky flame, and gave off suffocating vapours. Brogniart, director of the Royal Porcelain Works at Sèvres, being present was asked to explain it, and he requested his

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[1] *Leçons de Chimie.*

son-in-law, Dumas, to ascertain the cause. Dumas soon found that the candles contained chlorine, which had been used for bleaching the wax, and that it escaped during the combustion as hydrochloric acid.[1]

In a paper in which Dumas discusses, amongst other subjects, the formation of chloral, he states that by the action of chlorine upon oil of turpentine, hydrogen is removed and replaced by an equal volume of chlorine, and he adds that Gay-Lussac had found the same in the case of wax. These facts, as well as others observed by Gay-Lussac, Faraday, Wöhler, and Liebig, showed that chlorine had the power of abstracting hydrogen from certain bodies and replacing it atom for atom. This natural law or theory of substitutions deserved a special name, and Dumas proposed to call it *metalepsy* (*μετάληψις*, exchange).[2]

In his more elaborate memoir [3] he no longer used this term, and stated that in the transformation of alcohol, C_2H_6O, into chloral, C_2HCl_3O, an apparent exception existed. Yet this exception corresponded with his theory, according to which alcohol was a combination of water with a hydrocarbon. The chlorine first decomposed the water, and the oxygen thus liberated would combine with the hydrocarbon, forming the compound C_2H_4O, which would then be acted upon by chlorine in accordance with his theory. Other dehydrogenating bodies appeared to behave like chlorine. Oxygen, for example, converted alcohol, $C_2H_4 . H_2O$, into acetic acid, $C_2H_4O_2$, by first abstracting from the hydrocarbon two atoms of hydrogen, which escape as water, whilst for each of them half an atom of oxygen is added, forming the group C_2H_2O, which

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[1] *Ber. deutsch. chem. Ges.* 17, Ref. 667.

[2] *Mém. Acad.* 15, 548.

[3] *Ann. Chim. Phys.* (2) 56, 140.

remains in combination with the water already present in the alcohol. According to Dumas the easy transformation of alcohol into acetic acid thus found its first rational explanation.

The *empirical law of substitutions* he formulated later on as follows:[1]

1. If a body containing hydrogen is subjected to the dehydrogenating action of chlorine, bromine, iodine, oxygen, etc., for each atom of hydrogen, which it loses, it takes up one atom of chlorine, bromine, or iodine, or half an atom of oxygen.[2]

2. If the body besides hydrogen contains oxygen, the same rule holds good without modification.

3. If, however, it contains water, the latter first loses its hydrogen without replacement, and then only hydrogen is removed and replaced as stated above.

Dumas adds that his empirical law, like every good theory, rested on well-founded facts. Among the younger French chemists whose attention it attracted, the most conspicuous was Auguste Laurent. He accepted Dumas's view, and in 1835 stated that on comparing the action of chlorine, bromine, oxygen, or nitric acid on different bodies, the following conclusions, of which the first proposition belonged to Dumas, were arrived at—

1. If chlorine, bromine, oxygen, or nitric acid act on a hydrocarbon, each atom of hydrogen which is removed, is replaced by one equivalent of chlorine, bromine, or oxygen.

2. At the same time hydrochloric acid, hydrobromic acid, nitrous acid, or water are formed, which

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[1] *Journ. Pharm.* May 1834; *Traité de Chimie*, 5, 99.

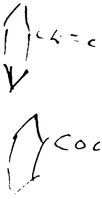
[2] Dumas and Berzelius took 16 as atomic weight of oxygen, while Liebig and most other German chemists used the equivalent 8.

are either set free or remain in combination with the newly-formed radical.[1]

A few months later he united these two propositions and set them forth without mentioning Dumas.[2] The latter returned to the subject on the occasion of Béchamp speaking of him *and Laurent* as the founders of the substitution theory. After discussing its historical development he says the statement of the fact that hydrochloric acid or water remained sometimes in the free state and sometimes remained in combination with the body formed by substitution, could not be regarded as a discovery. He had, as far back as January 13, 1834, explained the transformation of benzoyl hydride into benzoic acid as a substitution, hydrogen being replaced by oxygen, and the water formed remaining in combination with the benzoic acid. On August 11 of the same year Peligot and he had explained in the same way the oxidation of oil of cinnamon or cinnamyl hydride to cinnamic acid.

"We find here an exact application of the theory of substitution, which one of us has recently developed. Oil of cinnamon loses two atoms of hydrogen and gains one atom of oxygen, in order to form anhydrous cinnamic acid, as pointed out by theory. The water formed by this combustion combines with the anhydrous acid and converts it into the hydrate.

"I further stated in January 1834 that in the formation of chloral, the hydrochloric acid does not combine with it, whilst in the formation of benzoic acid the water produced does combine; wherefore it was unnecessary to discover in December 1835, that this might be so." [3]



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[1] *Ann. Chim. Phys.* (2) 60, 223. [2] *Ibid.* 326. [3] *Ibid.* (3) 49, 487.

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In the next year Laurent published his theory of organic compounds. These he considered to be derived from certain hydrocarbons, or primary radicals (*radicaux fondamentaux*). By replacing hydrogen by other elements, we obtain secondary radicals (*radicaux dérivés*), having physical and chemical properties much akin to those of the primary radicals. He further held the opinion that Dumas's rules were insufficient and did not always correspond to facts, inasmuch as in many cases a larger or smaller number of chlorine or oxygen atoms are added, than hydrogen atoms abstracted, even in the case of compounds containing no oxygen and consequently no water. The third rule of Dumas at any rate did not hold good. If, however, substitution of chlorine or bromine took place by equivalents, *these elements occupy the place of the hydrogen and play to some extent its part; and consequently the new body must exhibit analogies with the original substance.*[1]

From that time Laurent regarded the theory as belonging solely to him, saying that it had been objected to by some as absurd, while others stated he had borrowed it from Dumas. If it were to turn out a failure he would be held to be its author, but if a success, others would be said to have created it. If some said he had borrowed his ideas from Dumas, they might with equal reason say that Dumas had borrowed his theory from Liebig, who first showed that the hydrogen of benzoyl hydride can be exchanged for chlorine, or that Liebig had borrowed the same idea from the chemist who first found that the oxygen of potassium oxide can be exchanged for one equivalent

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[1] *Thèse de Docteur*, 1837 ; *Ann. Chim. Phys.* (2) 53, 384 ; *Méthode de Chimie*, 242 ; translated by Odling under the title, *Chemical Method.*

of chlorine, and that he again had borrowed it from Wenzel and Richter, and so on to Hermes and Tubal Cain.[1]

The first attack on the substitution theory came, of course, from Berzelius, who, however, by mistake ascribed Laurent's views to Dumas. They appeared to him detrimental to the progress of science by throwing a false light on objects and preventing chemists from seeing them in their correct shape. An element so highly electro-negative as chlorine could never enter an organic radical; such a view would be in opposition to the first principles of chemistry. When acting upon organic bodies this element formed new radicals and combined with them.[1]

Dumas replied that Berzelius attributed to him an opinion precisely contrary to that which he had always maintained, namely that chlorine takes *the place* of the hydrogen. "To represent me as saying that hydrogen is replaced by chlorine, which plays exactly the same part, is to attribute to me an opinion against which I protest most strongly, as it is in direct opposition to everything I have said on this subject. The law of substitutions is an empirical law; it expresses the relations between the hydrogen which goes away and the chlorine which goes in. I am not responsible for the exaggerated extension which Laurent has given to my theory."[2]

Laurent (of whom Berzelius said that he was blinded by his theory—a theory so bizarre, that it considerably diminished the value of his researches) was quite ready to take the whole responsibility for his views, maintaining as strongly as ever that, when

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[1] *Ann. Chim. Phys.* (2) 66, 326.

[2] *Ibid.* 67, 303.

[3] *Compt. rend.* 6, 647 and 695.

hydrogen is replaced by negative elements, such as chlorine or oxygen, the compounds thus formed exhibit a great analogy with the original body. From this Berzelius might draw whatever conclusions he liked; the facts which led to this theory could not be annihilated. Berzelius had made a mistake in assigning the theory to Dumas, and in order to exonerate the latter Laurent added that his theory was not an exaggeration of Dumas's but something quite different.[1]

When, however, by the researches of Laurent, Malaguti, and Regnault a considerable number of substitution products had been discovered, and Dumas himself had found that trichloracetic acid bears a greater resemblance to the original compound than any other known substitution product, he accepted Laurent's views. Laurent never acknowledged this, and in his *Chemical Method,* published only after his death in 1854, he endeavoured to prove that his theory and that of Dumas had nothing in common but the word substitution.

It has already been stated that Laurent published in 1836 a theory of organic compounds. This, though never generally received, has to be mentioned here because Gmelin made use of it in his handbook, with several alterations and extensions, for the classification of organic compounds.

According to Laurent every organic compound contains a nucleus (*noyau*). *Primary nuclei* (noyaux fondamentaux) consist of hydrocarbons. In these hydrogen can be replaced by other elements or groups of elements, *secondary nuclei* (noyaux dérivés) being thus formed. These substitution products resemble the original body, and this resemblance may be

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[1] *Ann. Chim. Phys.* (2) 72, 407.

explained by assuming that the primary nuclei have the shape of a prism, the carbon atoms being situated in the corners and the hydrogen atoms at the edges. On replacing the latter by chlorine the shape of the prisms is not altered, but if hydrogen be removed without replacing it, the prism falls to pieces, the compound undergoes decomposition.

To the prism may be added certain atoms or groups of atoms in the form of pyramids, or it may be surrounded by these; on removing them again, the original prism reappears.

According to Laurent all organic compounds contain an even number of atoms, and his formulæ are therefore sometimes double these now in use.

The following table, containing the compounds derived from etherene or olefiant gas,[1] may serve to illustrate his system. The principle of nomenclature, which will be readily understood, had been introduced by Dumas and Peligot, and was generally used by Laurent:—

Ethérène .	. C_4H_8
Hydrochlorate .	. $C_4H_8 + H_2Cl_2$
Chlorétherase .	. $C_4H_6Cl_2$
Hydrochlorate .	. $C_4H_6Cl_2 + H_2Cl_2$
Chlorétherèse .	. $C_4H_4Cl_4$
Hydrochlorate .	. $C_4H_4Cl_4 + H_2Cl_2$
Chlorétherise .	. $C_4H_2Cl_6$
Hydrochlorate .	. $C_4H_2Cl_6 + H_2Cl_2$
Chlorétherose .	. C_4Cl_8
Chloride ethérosique	$C_4Cl_8 + Cl_4$

These formulæ bear some resemblance to those of the aetherin theory, but have nothing in common with those of the radical theory, according to which, radicals always contain an uneven number of atoms.

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[1] *Ann. Chim. Phys.* (2) 63, 388.

It is noteworthy, as Ladenburg has pointed out,[1] that young Gerhardt, the future fellow-worker of Laurent, showed these formulæ to be untenable. Faraday had already found that Dutch liquid, Laurent's hydrochlorate of chloretherase, was converted, by the continued action of chlorine, into carbon sesquichloride or etherosic chloride. This proved that Dutch liquid did not contain hydrochloric acid, "if we would not maintain the absurdity, that chlorine decomposes hydrochloric acid in order to produce hydrochloric acid from it."[2]

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[1] *Entwickelungsgeschichte Chem.* 2nd ed. 162.

[2] Gerhardt, *Journ. prakt. Chem.* 15, 17.

III

Dumas's theory of types — Berzelius's coupled formulæ — Liebig's attack on the French chemists—Inverse substitution—Development of the radical theory—Liebig's theory of polybasic acids—Gerhardt and Laurent—Unitary formulæ.

DUMAS converted the substitution theory into a *theory of types*, formulating in 1839 the chief propositions as follows:[1]

1. The elements of a compound body can, in many cases, be replaced by equivalents of other elements or of compound bodies, which play the part of simple ones.

2. If such a substitution takes place equivalent for equivalent, the compound in which the replacement has occurred retains its *chemical type*, and the element or group which has been taken up, plays in it the same part as the element which has gone out.

Besides chemical types, such as acetic acid, $C_2H_4O_2$, and trichloracetic acid, $C_2HCl_3O_2$, aldehyde, C_2H_4O, and chloral, C_2HCl_3O, chloroform, $CHCl_3$, bromoform, $CHBr_3$, and iodoform, CHI_3, he also assumed, with Regnault, *molecular* or *mechanical types*. To these belong compounds containing the same number of equivalents, but exhibiting essentially different properties, such as alcohol and acetic acid.

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[1] *Ann. Chem. Pharm.* 33, 179 and 259.

Dumas further pointed out that the properties of a compound depended chiefly on the arrangement of its particles, and much less on their nature. He said that, according to Lavoisier, chemical combination took place by an element which supports combustion combining with a combustible element. This in the language of the electro-chemical theory was the combination of a negative and a positive element. Such a dualism was, however, not required for explaining the constitution of chemical compounds. We might compare them to a planetary system, and assume that their particles were kept together by their mutual attraction. They might be more or less numerous, simple or compound; in the constitution of bodies the simple ones played the part of the simple planets, Mars or Venus, and the compound ones that of our earth with the moon, or Jupiter with its satellites. If in such a system a particle were replaced by one of another kind, the equilibrium remained, and the new compound possessed properties resembling those of the original body so long as the particles removed and those which had replaced them resembled each other. If, however, they differed very much, the two bodies belonged to the same mechanical system, but a chemical similarity could be recognised only with difficulty.[1]

Berzelius could not accept such views. When in 1835 Laurent published his researches on the action of chlorine on naphthalene, Berzelius endeavoured in his Annual Report to prove that Laurent's compounds were chlorides of different hydrocarbons; and the year following he said of the nucleus-theory that it was of such a kind that it appeared superfluous to

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[1] *Ann. Chim. Phys.* (2) 73, 73.

report on it. When, however, Dumas threw down the gauntlet to Berzelius, there began an embittered controversy which lasted for years.

Dumas said in his memoir on chloracetic acid: "These electro-chemical conceptions, this special polarity, assigned to the atoms of simple bodies,—do they rest on such evident facts that they may be elevated to the rank of articles of faith? Or, if we regard them as hypotheses, have they at least the property of adapting themselves to facts, of explaining or anticipating them with such a certainty that in chemical investigations they have been found of much use?

"We must admit that such is not the case. What has been found in inorganic nature to be a useful and a true guide, isomorphism, is a theory which, as is well known, rests on facts, and which, as is equally well known, is little in accordance with the electro-chemical theory.

"Now in organic chemistry the theory of substitution plays the same part as isomorphism in mineral chemistry; and perhaps we may some day by experience find that these two general points of view are intimately related, being dependent on the same causes and capable of being comprised in a common expression.

"For the present, from the transformation of acetic acid into chloracetic acid, from that of aldehyde into chloral; from the fact that the hydrogen of these bodies is replaced by chlorine, volume for volume, without altering their original nature we must conclude:

"*That there exist in organic chemistry certain* TYPES *which remain as such, even after replacing their hydrogen by an equal volume of chlorine, bromine or iodine; i.e.*

the theory of substitution rests on facts, on the most striking facts of organic chemistry."[1]

From the war now waged by Berzelius and his followers against the adherents of the substitution theory, the latter emerged victorious; their views, in a more perfect form, but without essential change, prevailed, chiefly because one side had to recur to legions of new and more and more complicated hypotheses; while the other brought into the field a much more effective weapon,—a steadily-growing army of new discoveries.[2]

Berzelius understood from the beginning the bearing of Dumas's views. Dumas had stated plainly that the theory of substitution was incompatible with the electro-chemical theory and that the latter must be given up, as it did not help to predict the properties of compounds in so satisfactory a manner. According to Berzelius this meant "the downfall of the entire chemical structure as it now stands, and this revolution is to be brought about by the decomposition of acetic acid by chlorine under the influence of sunlight. It appears therefore not superfluous to throw more light on this compound, apparently so dangerous to the whole chemical edifice."[3] He came to the conclusion that the properties of acetic acid and chloracetic acid were totally different. The former contained the radical acetyl, while the latter was a combination of chloride of carbon with oxalic acid ($C = 6$, $O = 8$)[4]—

Acetic acid, $C_4H_3, O_3 + HO$,
Chloracetic acid, $C_2Cl_3 + C_2O_3 + HO$.

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[1] *Ann. Chem. Pharm.* 32, 101.

[2] Kekulé, *Lehrbuch*, 1, 69.

[3] *Ann. Chem. Pharm.* 31, 113.

[4] The older formulæ are here and in the sequel printed in italics.

Dumas said in his reply that Berzelius regarded the two compounds as different, because they had not the same density, the same smell, or the same boiling point. This was a mistake, for by the chief properties Dumas understood something quite different, namely, an analogous chemical behaviour. In the same way as trichloracetic acid was decomposed into carbonic acid and chloroform by heating it with an alkali, so acetic acid was resolved into carbonic acid and marsh gas, the latter being obtained artificially for the first time by this reaction. Chloroform must be regarded as one of its substitution products.[1]

In order to explain the constitution of the numerous substitution products discovered up to that time Berzelius was obliged to make use of very complicated formulæ. Thus dichlorformic ether (dichlorethyl formiate), $C_6H_4Cl_2O_4$ was, according to him, a combination of anhydrous formic acid with formylchloride, anhydrous acetic acid, and acetylchloride, $2C_2HO_3 + C_2HCl_3 + 2C_4H_3O_3 + C_4H_3Cl_3$; and the dichlorether obtained by Malaguti (Tetrachlorethyl oxide), $C_4H_3Cl_2O$, he believed to consist of anhydrous acetic acid, and acetylchloride, $C_4H_3O_3 + 2C_4H_3Cl_3$.[2]

These and similar formulæ could not find general acceptance. When Berzelius had sent his papers to Wöhler for translation, Liebig wrote: "Berzelius fights for a lost cause, and, quite against his nature, with the pen only. . . . I entreat you, dear Wöhler, to intervene in the interest of our old and highly-honoured friend, that he may not make himself a laughing-stock through us. It is horrible to think that the time must come, when we can believe only in the past as true, and

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[1] *Ann. Chem. Pharm.* 33, 179 and 187.

[2] *Ibid.* 32, 72.

regard the future as only froth and phantasy; when with all our might, we must cling to that which exists, because we have no longer the power to keep pace; and yet the wheel of time cannot stand still. But if you insist upon it, it shall be printed."[1]

In a note to Berzelius's first paper, Liebig says, he could not share the views of Berzelius, because they rested on a number of hypothetical assumptions, for which every kind of proof was wanting:—

"We have made in inorganic chemistry the singular observation that the manganese of permanganic can be replaced by chlorine, without changing the form of the compound, which permanganic acid forms with bases. Yet there is hardly a greater dissimilarity known than that existing between the chemical properties of chlorine and manganese. Such facts are beyond discussion; we must take them for what they are; chlorine and manganese can replace each other in certain compounds without the nature of the compound being changed. I cannot conceive, why a similar behaviour should be found impossible for other bodies, for chlorine and hydrogen for example, and the conception propounded by Dumas appears indeed to form the key to most phenomena in organic chemistry."[2]

Again he says: "Berzelius, many years ago, pointed out the analogy existing between organic and inorganic compounds. He was the first who regarded organic acids, ether, etc., as oxides of compound radicals; this view was a guiding star in a labyrinth, where nobody would find his way. We cannot and must not abandon this safe guide in cases where it

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[1] Liebig and Wöhler's *Briefwechsel*, 1, 147.

[2] *Ann. Chem. Pharm.* 31, 119.

gives light and clears up the unknown; but if organic compounds, looked at in a certain direction, resemble inorganic ones, yet in ever so many respects they differ—they possess peculiarities which we must be content to acknowledge as we cannot explain them. Thus we are led to further views, and our conceptions are expanded and perfected. We follow therefore the principles of inorganic chemistry to a certain point, but beyond it, where they abandon us, where instead of solving difficulties they create them,—beyond this point we require new principles. This alone is the cause of the difference in our opinions."[1]

On the other hand, Liebig attacked the French chemists; first of all Dumas, as going too far in assuming that even carbon followed the law of substitution. Walter had found that on heating camphoric acid, $C_{10}H_{16}O_4$, with sulphuric acid it was converted into sulpho-camphoric acid, $C_9H_{16}SO_6$, from which Dumas concluded that in its formation one atom of carbon was replaced by sulphur dioxide, writing its formula, $C_9(SO_2)H_{16}O_4$.[2]

In Liebig's *Annalen* there appeared in 1840 a letter dated from Paris, in which the chemical public was informed that the writer has succeeded in replacing in manganese acetate, not only the hydrogen by chlorine, but also the metal, and finally the carbon and oxygen too; the product, although consisting of chlorine only, exhibited all the characteristic properties of the original salt. The writer continued:

"Quoique je sache, que dans l'action décolorante du chlore il y a remplacement de l'hydrogène par le

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[1] *Ann. Chem. Pharm.* 32, 72.

[2] Dumas, however, never recurred to this subject.

chlore et que les étoffes, qu'on blanchit maintenant en Angleterre, d'après les lois des substitutions conservent leur types, je crois néanmoins que la substitution du carbone par le chlore, atome pour atome, est une découverte qui m'appartient."

A note is added: "Je viens d'apprendre qu'il y a déjà dans les magasins à Londres des étoffes en chlore filé, très recherchées dans les hôpitaux et préférées à toutes autres pour bonnets de nuit, caleçons, etc."

Liebig, who could handle the weapon of satire so skilfully, was believed to be the author of this letter, signed S. C. H. Windler[1] (*anglicè* S. Windler), until it was found that the idea originated with his friend Wöhler, who, on the 10th of February 1840, wrote to Berzelius: "The chemical bother and talk, the eternal song of the substitutions makes one quite sick. And how many of the statements . . . are only guesswork, only assertions, and yet put down as facts. J'ai découvert un des faits les plus éclatants de la chimie organique. J'ai vérifié la théorie des substitutions d'une manière extrêmement remarquable et parfaitement inattendue. C'est seulement dès à présent qu'on pourra apprécier la véritable valeur de cette théorie sublime et glorieuse. Voilà le fait inoui sans semblable dans l'histoire de la chimie."

He proceeds to say that by passing chlorine in the sunlight into a solution of copper acetate, he obtained, as was to be expected, the copper salt of Dumas's chloracetic acid. On heating this in a current of dry chlorine oxygen was liberated, a yellowish mass being formed, consisting of chloro-copper chloracetate. On continuing the action of chlorine the metal was also replaced, and chlorine chloracetate was formed, crystal-

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[1] *Ann. Chem. Pharm.* 33, 308.

lising in small brilliant golden yellow prisms. This was, however, not the final product, inasmuch as by treating it in an aqueous solution with chlorine for two weeks longer, carbonic acid was evolved, and on cooling the liquid to 2° it deposited crystals, having all the properties of chlorine hydrate. "Ainsi c'était la substitution la plus parfaite du monde, c'était de l'acétate cuivrique hydraté, dans lequel tous les éléments du sel étaient substituées par le chlore.—But enough of this nonsense."

In another letter Wöhler explains how it happened that the letter was published. It occurred to him to send the skit to Liebig, and to copy it in the form of a letter dated from Paris, without thinking in the least that Liebig, who had made some alterations and added a few witticisms, would be so rash as to publish it.[1]

Facts now rapidly increased which went to prove the correctness of the theory of substitution, as far as the replacement of hydrogen was concerned, and the products thus formed were found to possess the fundamental properties of the original compound. Of still greater importance was the discovery that these products could, by inverse substitution, be reconverted into the original compound. Melsens found in 1842, that by the action of potassium amalgam on an aqueous solution of trichloracetic acid, its chlorine was replaced completely by hydrogen, acetic acid being reproduced.[2]

These and similar facts, however, did not shake Berzelius's faith. He said: "If we remember the

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[1] *Bruchstücke aus den Briefen Wöhler's an Berzelius*, p. 48. Berlin 1884.

[2] *Ann. Chim. Phys.* (3) 10, 233.

decomposition of the acid by chlorine into chlorocarbonoxalic acid, another view of the composition of acetylic acid presents itself as possible, viz. that it might be a coupled oxalic acid, its copula being C_2H_3, just as C_2Cl_3 is the copula of chloro-carbonoxalic acid; consequently the action of chlorine on acetylic acid consists in the transformation of the copula C_2H_3 into C_2Cl_3.[1] He assigned, therefore, to acetic acid the formula $C_2H_3+C_2O_3+HO$. In a similar way he wrote the formulæ of other bodies capable of undergoing substitution; they all contained a *copula*,[2] consisting of carbon and hydrogen, and only the latter could be replaced by chlorine, etc.

In the year 1845 Hofmann discovered the substituted anilines, endowed, like aniline itself, with basic properties, which, however, became weaker in proportion as hydrogen was replaced. He said that from his observations it appeared without doubt that chlorine or bromine could play the part of hydrogen in organic compounds, taking their electro-negative character with them into the new compounds, and impressing it the more strongly upon them, the greater the number of hydrogen atoms replaced by the halogens. Liebig adds: "The author seems to have definitely proved that the chemical nature of a compound does not in any way depend upon the nature of the elements contained in it as is assumed

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[1] *Lehrb.* 5th ed. p. 460 and 709. This view was never generally accepted, and afterwards almost given up, until it was revived again in a new and improved form. We write now the formula of acetic acid, $CH_3.CO_2H$, or regard it as a linking of methyl with carboxyl or half a molecule of oxalic acid. This example shows that the development of chemistry takes place according to the law of dialectic.

[2] This term was first employed by Gerhardt, but in a different sense, as will be shown later on.

by the electro-chemical theory, but entirely on their arrangement."[1]

To this Berzelius replied that all organic bases were coupled ammonias, thus aniline was $C_{12}H_4$, NH_3, and chloraniline, $C_{12}H_3Cl$, NH_3; both contained ammonia as the basic constituent, the composition of the copula being of no consequence. He was so convinced of the correctness of this view that he could not understand how anybody could hold another opinion. He did not see that he had accepted the substitution theory. In his joy over the discovery of the copula he had completely forgotten that originally the object of his opposition had been to combat Laurent's view, according to which chlorine could replace hydrogen and take over its functions. What formerly appeared absurd became now "surprisingly clear and simple." From this time Berzelius's opposition to the theory of substitution began to grow lame. Wöhler says in a letter to Liebig, dated 8th January 1841: "Berzelius writes, 'I am now in that period of life where only the memory of previous times remains, but that which happened yesterday or the day before is completely forgotten. For this reason I am only fit for such simple researches as can be completed within a few days, and which do not require me to remember complicated details.' Is this not a sad confession?"[2]

When in 1827 Berzelius developed the electro-chemical theory, he said prophetically:

"The habit of an opinion often leads to the complete conviction of its truth; it hides the weaker parts, and makes us incapable of accepting the proofs against it."

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[1] *Ann. Chem. Pharm.* 53, 1.

[2] Liebig and Wöhler's *Briefwechsel*, 1, 169.

This was the case with Berzelius in 1845; his formulæ became more and more complicated; he was obliged to introduce an endless number of utterly hypothetical radicals, and after his death (1848) his followers had the greatest difficulty in reconstructing radicals anew out of his copulæ.[1]

Meanwhile the radical theory had made great progress. Bunsen showed in his classical researches on the cacodyl compounds that they contain the radical AsC_2H_6, possessing all the properties of a metal and capable of existing in the free state. He justly says that it plays in its minutest details the part of a simple electro-positive element, *that it is a true organic element.*[2]

From 1848 onwards, Kolbe and Frankland succeeded in preparing a series of hydrocarbons, which according to their mode of formation and their empirical formulæ were regarded as free alcohol radicals.

Döbereiner again had found that oxalate of ammonia was resolved by the action of heat into water and cyanogen, whilst formate of ammonia yielded prussic acid, which on heating with caustic potash was again transformed into formic acid. Kolbe and Frankland regarded the latter as oxalic acid coupled to hydrogen, whilst acetic acid and its homologues contained alcohol radicals in place of the hydrogen. If this hypothesis were correct, acetic acid would be formed by heating cyanide of methyl with caustic potash: and this was confirmed by experiment. In a similar way they succeeded in obtaining other fatty acids from the cyanides of the alcohol-radicals.[3]

[1] Kekulé, *Lehrb.* 1, 75.

[2] *Ann. Chem. Pharm.* 42, 27.

[3] *Ibid.* 65, 288.

Kolbe next tried to decompose acetic acid by the galvanic current, expecting that he would obtain at the positive pole carbonic acid as an oxidation-product of oxalic acid, and that at the negative pole a compound of methyl and hydrogen, *i.e.* marsh gas would be evolved. "The decomposition, however, did not take place as expected, yet as the following experiments show, the results are none the less interesting and they deserve still greater attention, for they open the prospect of obtaining important information as to the constitution of organic compounds by means of their electrolytic decomposition."

He found that at the negative pole only hydrogen was evolved, while at the positive a mixture of carbonic acid and a gas having the composition of methyl was obtained, products which he regarded as being formed by the action of oxygen on methyloxalic acid.[1]

Liebig had anticipated that the alcohol-radicals would be isolated by the action of potassium on their iodides. Frankland, using zinc, did obtain them, and discovered at the same time their important combinations with zinc.

These discoveries were hailed with great joy by the adherents of the radical theory, and although it was afterwards found that these hydrocarbons were not the free radicals, their further investigation contributed much to the development of organic chemistry.

The old question whether a radical could contain oxygen was still discussed. Berzelius had opposed such a view, saying, as far back as 1843, that it was as inadmissible as the assumption that sulphurous acid was the radical of sulphuric acid, or manganese peroxide that of manganic acid. "*An oxide cannot be a radical.*

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[1] *Ann. Chem. Pharm.* 69, 279.

The conception involved in the term radical implies this, that the word means a body which in an oxide is combined with oxygen.

The introduction of the theory of substitution into the radical theory led to the conception of substituted radicals. Now if chlorine can replace hydrogen, without essentially changing the properties of a compound, why should not oxygen do so? The radical theory was never in want of hypotheses, and some of its adherents went so far as to assume that on chlorine replacing hydrogen or *vice versâ*, the electro-chemical properties of both, or at least one of them, underwent a change.

The further development of the theory of substitution and of types led to a more precise definition of "a substitution product," and a clearer conception of the terms: *Equivalent*, *Atom*, and *Molecule*.

According to the dualistic theory a neutral salt had a very simple constitution. It consisted of one "atom" of base united to one "atom" of acid. A base was a metallic oxide in which there was supposed to be, as a rule, one atom of metal to one atom of oxygen. An acid was a non-metallic oxide containing one atom of a non-metallic element. Thus the base soda was NaO, the acid sulphuric acid was SO_3, hence neutral sulphate of soda was $NaO . SO_3$. In the same way calcium sulphate was $CaO . SO_3$. The compound of SO_3 with water which we now call sulphuric acid was regarded as a hydrate of the true acid SO_3 and was written $SO_3 . HO$. In a similar way potassium hydrogen sulphate was regarded as $KO . SO_3 + SO_3 . HO$, *i.e.* a hydrated acid sulphate or bisulphate of potash.

This simple representation of salts was not possible in the case of phosphoric acid. Graham had shown that there were three essentially different phosphoric acids, and that the difference was to be seen in the different oxygen ratio of their salts. The ratio of the oxygen of the base to the oxygen in the acid in the orthophosphates was 3 : 5, in the pyrophosphates 2 : 5, and in the metaphosphates 1 : 5. The idea of "basicity" of acids was thus introduced. But more important than this was the conclusion that in the orthophosphates water might play the part of a base. Common phosphate of soda, $2NaO \cdot PO_5 \cdot 25HO$, was found to lose $\frac{24}{25}$ of its water at the temperature of boiling water and still to retain its ordinary chemical properties. On losing the last atom of water at a much higher temperature a salt (pyrophosphate) with different chemical properties was obtained. This last atom of water was, therefore, regarded by Graham as determinative of the chemical character of the salt and to play in fact the part of a base. Such a view explained very simply the otherwise unaccountable fact that ordinary phosphate of soda gave with silver nitrate, a salt, $3AgO \cdot PO_5$ and free nitric acid. According to Graham's view, then, we must write the following formulæ for the orthophosphates :—

Phosphoric Acid.	Acid Salts.		Neutral Salt.
$PO_5 \cdot 3HO$	$PO_5 \cdot 2HO \cdot NaO$	$PO_5 \cdot HO \cdot 2NaO$	$PO_5 \cdot 3NaO$

In the acid salts the water was very different from the loosely attached water of crystallisation; it had a "constitutional" function.

About the same time, a discussion took place between Berzelius and Liebig as to the formula of citric acid and the citrates; and in 1838 Liebig[1] published his well-known memoir on the constitution

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[1] *Ann. Chem. Pharm.* 26, 113.

of organic acids. In this he developed Graham's idea of the basicity of acids and applied it to a large number of organic acids, showing that like phosphoric acid they could unite with one, two, and three equivalents of base. He also gave a criterion for the determination of the basicity of an acid,—a polybasic acid must be able to form salts containing more than one base. Thus ordinary phosphate of soda, $PO_5 . 2NaO . HO$, on addition of potash gave $PO_5 . 2NaO . KO$, and tartaric acid gave Rochelle salt, $C_8H_4O_{10} . KO . NaO$.

This criterion, which we now know to be faulty, led Liebig into some difficulties. Since, for example, acid sulphate of soda, $SO_3 . NaO + SO_3 . HO$, on addition of caustic potash did not give a double salt, but the separately crystallisable sulphate of potash and sulphate of soda, he had to regard sulphuric acid as a monobasic acid, and the acid sulphate of soda as a salt of a different order from ordinary phosphate of soda. Notwithstanding this, Liebig's investigations gave wide currency and application to the doctrine of basicity.

So far we have spoken only of oxyacids. It must, however, be remembered that since the elementary nature of chlorine and the absence of oxygen in hydrochloric acid had been established, acids had been divided into two classes—oxyacids and hydracids according to whether or not they contained oxygen. Davy had opposed this classification, denying the propriety of ascribing "acidifying" properties to any one element. He had pointed out that, both in the hydracids and hydrated oxyacids of chlorine and iodine, hydrogen occupied a place corresponding to that of the metal in the saline derivatives. Dulong had insisted on the same view, regarding acids as compounds of hydrogen with certain elements or groups of elements. This theory, which implied the existence of such groups as SO_4, NO_6, etc., was supposed to be utterly incompatible with the dualistic theory, and after a vigorous opposition had sunk into abeyance. It was now revived by Liebig. He pointed out that Davy's argument as to the analogy between the constitution of acids and salts might be extended to sulphuretted hydrogen, sulphurous acid, sulphuric acid, phosphoretted hydrogen, phosphorous acid, and phosphoric acid, and that in general acids might be regarded as compounds of hydrogen in which this element could be replaced by metals so as to form salts. He says:

"These bodies, which at present are called anhydrous acids, acquire the property of forming salts with metallic oxides in most cases only by the addition of water, or they are compounds which attack oxides at a high temperature only.

"When an acid is added to a metallic oxide, the hydrogen generally separates in the form of water. So far as the constitution of the new compound is concerned it is quite immaterial how we imagine the formation of this water to take place; in many cases it may be formed by the reduction of the oxide, in others at the expense of the elements of the acid—we do not know."

"All we know is that without water no salt can be formed at the ordinary temperature, and that the constitution of the salt is analogous to that of the hydrogen compounds which we call acids."

He goes on to show that many organic acids must be regarded as hydracids, and that though this view cannot be extended to the inorganic acids, as it would involve the supposition of a number of hypothetical radicals, which could not be isolated, such as SO_4, "This objection is of little significance in organic chemistry; all organic acids, excepting two or three, are just such hypothetical bodies; they are as unknown as the radicals to which Davy's view leads. Anhydrous oxalic acid, acetic acid,[1] etc., are mere conceptions; the so-called anhydrous organic acids have lost their capacity for saturation."

In conclusion he says that the conception of organic acids as hydracids had given him an insight into their constitution, and he adds:—"We have cause to ask: is this view to be taken as true, because it is likely to lead to discoveries? An answer is not easy; on testing and applying a new theory, we must take care not to be bribed by the results it offers. Every view invites us to test it, to confirm it. It leads to experiments, to work. But in working we are always sure to make discoveries, no matter whence we start."

The theory of hydracids did not replace the older one, but made its appearance again later on in a new form.

The theory of polybasic acids was further developed by Laurent and Gerhardt, whose names will always remain inseparable in the history of our science. With indomitable perseverance they worked towards one great end: that of removing those older views on the constitution of chemical compounds, which they had recognised as incorrect and of replacing them by others more in accordance with facts. By their ingenious speculations on the relative weights of atoms and molecules, these terms were first precisely defined,

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[1] Liebig meant, of course, $C_2H_2O_4 - H_2O$ or C_2O_3 and $C_2H_4O_2 - H_2O$ or C_2H_2O, corresponding to $H_2SO_4 - H_2O$ or SO_3, etc., the anhydrous inorganic acids as they were termed.

and almost every argument they used holds good to this day. They took the foremost place in erecting the present chemical system, by developing Liebig's views and consistently working them out.

According to Gerhardt an acid was bibasic if it formed acid salts or double salts with any base, or contained two or more atoms of hydrogen replaceable by metals. But the most characteristic property of such an acid he found in the fact that it could form several compound ethers, one atom of hydrogen after the other being replaced by an alcohol radical. Laurent added as another characteristic that a polybasic acid could form two or more amido-compounds.

They expressed the formulæ of the salts and ethers as belonging to the same type as the acid itself; and still using the old equivalent weights, they wrote the following formulæ :—

Sulphuric acid	$H_2S_2O_8$
Neutral potassium salt	$K_2S_2O_8$
Acid potassium salt	KHS_2O_8
Neutral ether	$(C_4H_5)_2S_2O_8$
Acid ether	$(C_4H_5)HS_2O_8$

We find here one of the first attempts to ascertain the relative weights of different molecules by a conformable interpretation of similar chemical phenomena. This method was generally employed by Laurent. He showed, for example, that the molecule of chlorine must consist of two atoms, inasmuch as by its action upon organic compounds always 2, 4, 6, etc., atoms came into play. He arrived at the same conclusion by comparing the action of chlorine with that of organic chlorides, such as cyanogen chloride, benzoyl chloride and others, which, under certain conditions, underwent analogous changes, showing that if a molecule of these chlorides could be divided into two parts, the same must hold good for chlorine itself.

Gerhardt, on the other hand, founded his speculations chiefly on Avogadro's law, according to which equal volumes of different gases at the same temperature and pressure contain the same number of molecules. The relative molecular weights of gaseous or readily volatile bodies could thus easily be ascertained, and therefore also the true atomic weights, if we define a molecule as the smallest quantity of an element or a compound existing in the free state and an atom the smallest quantity of an element occurring in a molecule. Resting his speculations at the same time, like Laurent, on chemical analogies, he arrived at the conclusion that the atomic weights of oxygen, sulphur, carbon, etc., hitherto in use, must be doubled, and that the molecules of hydrogen, oxygen, and other elements consisted of two atoms.

The activity and merits of these two men were so little recognised during their own lifetime that Gerhardt alone just lived long enough to see their views generally accepted.

When in 1843 Gerhardt proposed to double the atomic weights of oxygen, sulphur, and carbon, Berzelius found the proposal so absurd that it appeared to him unnecessary even to mention it in his Jahresbericht.

To give a sound foundation to their theories, Laurent and Gerhardt made a number of important researches. But their results when correct found little acknowledgment, and when erroneous were judged very harshly. It is true that their great talent for regarding a number of facts from a single point of view led them sometimes astray; some of their assertions rested more on theoretical speculation than on experimental observation; consequently their views were too often rejected as being confused or unscientific. Liebig attacked them vigorously; but being treated without consideration, and being convinced of the truth of their views, their retorts were as inconsiderate as the attacks.[1] The provoking tone in which they condemned the older views, and the assurance with which they brought forward their own, gave great offence, and subjected these two great chemists to treatment which it is now quite painful to think of.[2]

To keep chemistry free from all fictions, they employed at first only empirical formulæ, or such as simply expressed the composition of a molecule; because, as Laurent said, the adherents of the radical theory had made chemistry a science of non-existent bodies. Liebig's satire on the theory of substitution Laurent repaid by the announcement of a newly-discovered radical, which he called *Eurhyzen* (εὖ, beautiful; *ῥίζα*, a root), which fulfilled all the functions of such a body, and yet was nothing but hydrogen peroxide. When to-day we look back on such discussions and controversies they appear strange enough. Berzelius tried to ridicule the notion of radicals containing oxygen by saying we might as well regard sulphur dioxide as the radical of sulphuric acid. To-day we hold exactly this view, regarding the acid as a combination of sulphur dioxide or sulphuryl, SO_2, with two half molecules of hydrogen peroxide or hydroxyl, HO,—these

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[1] *Ann. Chem. Pharm.* 57, 93, 388; 58, 227.

[2] Kopp, *Entwicklung Chem. neu. Zeit.* 628.

groups fulfilling all the conditions of a compound radical as defined by Liebig.

The use of empirical or *unitary* formulæ, as they were called, in contrast to the *binary* or dualistic formulæ of Berzelius, was an advance, because now any compound containing more than two elements appeared as a chemical whole, and not as being made up of different proximate constituents, each of which formed a closed group of atoms. The common features of analogous compounds could be more clearly seen, and the facts directly compared with each other, instead of being looked at through the deceptive glass of inherited hypotheses.[1]

Certain groups of compounds could now be arranged from a single point of view, and their composition expressed by a general formula such as $C_mH_nO_o$. By these means the chemical changes which the members of a group underwent might be represented by general equations, such as Laurent and Gerhardt had used, and which had previously been ridiculed as chemical algebra.

The use of unitary formulæ had, however, a drawback; it was found that they did not represent the relations of different compounds to each other as clearly as did the formulæ based on the radical theory. Laurent and Gerhardt employed, therefore, so-called synoptical formulæ. In these a group of atoms, remaining together throughout a number of changes. was written separately or expressed by a symbol. Such formulæ sometimes resembled those of the theory of radicals, sometimes those of the nucleus theory; their sole purpose was to exhibit in a clear way the mutual relations of the various bodies.

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[1] Kekulé, *Lehrb.* 1, 84.

IV

Introduction of the radicals into the types — Liebig's views on radicals — Theory of residues — Discovery of the compound ammonias by Wurtz and Hofmann — Williamson's water type — Gerhardt's Theory of types — Condensed types — Coupled compounds — The beginning of the theory of valency.

THE next great advance was the introduction of the radicals into the types, leading gradually to an amalgamation of the two theories. Dumas had already called attention to the fact that not only elements, such as chlorine, but also groups of atoms, such as NO_2, could replace hydrogen in a compound, and that these deserved the name of compound radicals. Gerhardt adopted this view in 1839, but did not admit, like the adherents of the radical theory, that such a group formed a chemical whole, or was a proximate component of a compound. This latter view had, however, already been opposed by Liebig, who said in 1835: "We may hope that the time is not far distant, when in organic chemistry the idea of unchangeable radicals will be given up."[1] In the next year he developed his views more fully, saying: "The idea of unchangeable radicals has recently become dominant in organic chemistry; I have already stated as my opinion that we cannot apply it to all

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[1] *Ann. Pharm.* 14, 166.

organic compounds; for as certainly as we never can produce sulphuric acid or phosphoric acid from matter containing neither sulphur nor phosphorus, as surely do I hold that the production of a vegetable acid does *not* require the prior formation of an organic radical. Formic acid and acetic acid are produced under the most varying conditions, which, considered by themselves, completely exclude the idea of a radical. I believe that benzoic acid can be formed without its radical benzoyl being formed precedently to the higher oxide. But when the components once have united to form a compound, we must assume that the elements are arranged in exactly the same manner, howsoever the compound may have been produced. We shall never be in a position to assume that carbonic oxide attains pronounced acid properties by combining with water. From the two we obtain one of the most powerful acids; but it is impossible that formic acid contains water as such. In this sense we shall always speak of the radicals of formic acid, of acetic acid, of benzoic acid, and if we wish to establish a theory of the formation of acetic acid from *alcohol*, or of benzoic acid from *oil of bitter almonds*, every view has to be excluded if it does not start in the first case from aldehyde and in the second from benzoyl."[1]

The question whether ether was an oxide of ethyl or a combination of olefiant gas and water was not settled in 1839. Dumas and Boullay had shown that the latter hypothesis allowed the derivatives of alcohol to be compared with the compounds of ammonia (p. 19). Discussing this subject Liebig said: "If we compare from our present standpoint the ammonia-compounds with the ether-compounds, we readily

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[1] *Ann. Chem. Pharm.* 18, 323.

perceive that the opposing views were fundamentally identical. We combated each other, because we could not agree upon the interpretation of the phenomena. If we regard *Amide* as the unvarying radical of the ammonia-compounds, and *Acetyl* as the starting-point of the ether-compounds, both groups assume the same form."

The compounds of both differ only in so far as acetyl possesses the property of forming acids, whilst in ammonia this property is wanting. If we call *Ad* the compound N_2H_4 = Amide, and *Ac* the compound C_4H_6 = Acetyl, we have—

ACETYL-COMPOUNDS.

$Ac = C_4H_6$ = Acetyl
AcH_2 = Olefiant gas
AcH_4 = Ethyl
AcH_4O = Ether
AcH_4Cl_2 = Ethyl chloride
AcH_4O + 1 atom of acid = Salts of ethyl oxide

AMIDE-COMPOUNDS.

$Ad = N_2H_4$ = Amide
AdH_2 = Ammonia
AdH_4 = Ammonium
AdH_4O = Ammonium oxide
AdH_4Cl_2 = Salammoniac
AdH_4O + 1 atom of acid = Salts of ammonium oxide

There exists also a number of other examples, such as—

Acetyl chloride	$AcCl_2$
Acetic acid	$AcO + O_2$
Hydrated acetic acid	$AcO + O_2 + H_2O$

In conclusion he says: "The above formulæ do not require any explanation; they have been developed in order to show the striking similarity between the compounds of ether and those of ammonia, andto point out why many chemists regarded olefiant gas as the first member of the ether-compounds. It is easily seen that both theories, formerly opposed to each other, have, from this point of view, the same foundation, and the problem as to which is true, has solved itself."[1]

In the same year Gerhardt published his views on the process which takes place when an element is replaced by a group of atoms. He did not consider it as a substitution but as a union of two residues to a unitary whole, and not an articulated binary compound. Those groups of atoms which till then had been called compound radicals, he named "*le reste*" or "*le restant*," and later on he developed his "*théorie des résidus*." According to this a residue could have the composition of a compound radical, but was not present as such in a compound. The radical theory regarded ethyl nitrate as a compound of anhydrous nitric acid with ethyl oxide; its formula expressed by equivalents being C_4H_5O, NO_5. It is produced by the action of nitric acid on alcohol—

$$C_2H_6O + HNO_3 = C_2H_5NO_3 + H_2O$$

Now, according to Gerhardt, the reaction consisted in one of the compounds giving off one atom of hydrogen and the other the residue OH, which combined together, forming water, while the two other residues formed the unitary ethyl nitrate.

By the action of ammonia on benzoyl chloride we

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[1] *Ann. Chem. Pharm.* 30, 138.

obtain benzamide, a reaction which Gerhardt expressed by the equation—

$$Cl(C_7H_5O) + NH_3 = NH_2(C_7H_5O) + ClH$$

On heating benzamide with potash, it is converted into potassium benzoate—

$$NH_2(C_7H_5O) + KOH = KO(C_7H_5O) + NH_3$$

Each molecule is split into two parts, and the residues unite in such a way that a *mutual decomposition* or a *double exchange* takes place. Almost all, and even the most simple chemical reactions, such as the formation of hydrochloric acid from hydrogen and chlorine, must be regarded as such double decompositions, each molecule being first resolved into two parts, whereupon the residues unite.

Gerhardt says: "J'appelle radicaux ou résidus les éléments de tout corps qui peuvent être ainsi transportés dans un autre corps par l'effet d'une double décomposition, ou qui y ont été introduits par une semblable réaction. Ainsi le chlorure de benzoïle, l'acide benzoïque, la benzamide, renferment le radical C_7H_5O (benzoïle); l'ammoniaque, l'eau, la potasse, renferment le radical H (hydrogène)."

After having further discussed this point, he adds: "On voit, d'après cela, que, contrairement à la plupart des chimistes, je prends l'expression de radical dans le sens de rapport, et non dans celui de corps isolable ou isolé."

He therefore makes a distinction between the radical hydrogen and the gas hydrogen, between the radical chlorine and the gas chlorine. These elements are obtained in the free state by double decompositions, and can again take part in such, just as benzoyl hydride or benzoyl chloride can.[1]

Gerhardt's conception of radicals soon supplanted the older views, and its introduction into the theory of types led to a fusion of both theories.

The first step in this direction was the discovery of the compound ammonias by Wurtz in 1849.[2] The preparation of such compounds had been predicted by Liebig's wonderful acuteness. He said: "If it were possible in the oxides of ethyl and methyl, in the oxides of bibasic acids, to replace the oxygen by one equivalent of amide, we should, without the least doubt, get compounds having the greatest resemblance to ammonia. Or expressed by a formula, a compound $C_4H_{10} + N_2H_4 = \mathrm{Ac} + \mathrm{Ad}$ would have basic properties."[3] Wurtz adopted this formula for his "*éthyliaque*," which name Hofmann afterwards changed into ethylamine. In the same way Liebig regarded aniline as a compound of amide with the radical $C_{12}H_{10}$. According to Berzelius, all organic bases were coupled ammonias.

Hofmann discovered another method of preparing the bases obtained by Wurtz, and showed by a series of elaborate experiments that in them, as well as in aniline, the two hydrogen atoms of the amide could be replaced by alcohol radicals. We must, therefore, look upon these compounds as ammonia in which the hydrogen is partly or wholly replaced by radicals, as the following formulæ show:—[4]

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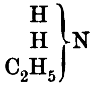
[1] *Traité Chim. Org.* 4, 568.

[2] *Ann. Chem. Pharm.* 71, 330.

[3] *Handwörterb.* 1, 699.

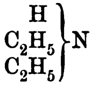
[4] *Ann. Chem. Pharm.* 73, 91; 74, 1.

Ethylamine.



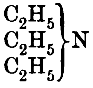
$$\left.\begin{matrix}H\\H\\C_2H_5\end{matrix}\right\}N$$

Diethylamine.



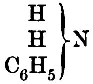
$$\left.\begin{matrix}H\\C_2H_5\\C_2H_5\end{matrix}\right\}N$$

Triethylamine.



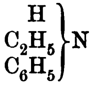
$$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}N$$

Aniline.



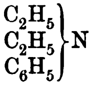
$$\left.\begin{matrix}H\\H\\C_6H_5\end{matrix}\right\}N$$

Ethylaniline.



$$\left.\begin{matrix}H\\C_2H_5\\C_6H_5\end{matrix}\right\}N$$

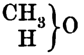
Diethylaniline.



$$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_6H_5\end{matrix}\right\}N$$

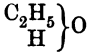
Williamson then showed in 1850 that in an analogous manner the alcohols and their ethers could be referred to the type *water*. If we replace in a molecule of the latter one atom of hydrogen by an alcohol radical, we have an alcohol. In this the second atom of hydrogen can be exchanged, and an ether is formed. He gave the following formulæ—

Methyl alcohol.



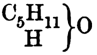
$$\left.\begin{matrix}CH_3\\H\end{matrix}\right\}O$$

Ethyl alcohol.



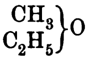
$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$$

Amyl alcohol.

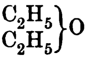


$$\left.\begin{matrix}C_5H_{11}\\H\end{matrix}\right\}O$$

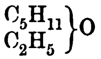
By replacing the hydrogen by ethyl, he prepared the following ethers—



$$\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}O$$



$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$$



$$\left.\begin{matrix}C_5H_{11}\\C_2H_5\end{matrix}\right\}O$$

At the same time he discovered the important fact, that in order to obtain the first of these compounds we can start either with methyl alcohol or ethyl alcohol, while the last may be prepared from ethyl alcohol or from amyl alcohol.[1]

Williamson further pointed out that acetic acid,

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[1] *Brit. Assoc. Rep.* 1850, 55 ; *Quart. Journ. Chem. Soc.* 4, 106.

which is formed by replacing in ethyl alcohol one-third of its hydrogen by oxygen, must have a constitution similar to that of alcohol. That an acid is thus produced we can readily understand, for we know a number of examples showing that the acid character of a compound is intensified, or its basic character is weakened, when hydrogen is replaced by an electro-negative element or radical. Phenyl alcohol (phenol), C_6H_6O, has weak acid properties; if we substitute hydrogen by hyponitric acid (nitroxyl), NO_2, we obtain bodies with more and more pronounced acid properties, the last being carbazotic or picric acid (Trinitrophenol), $C_6H_3(NO_2)_3O$. Hofmann showed that the basic properties of aniline were weakened by chlorine-substitution until they disappeared completely in trichloraniline.

Since Berzelius regarded acetic acid as a compound of the radical C_2H_3, which he called acetyl, Williamson proposed to call the radical C_2H_3O, which is obtained from ethyl by oxygen-substitution, *Oxygen-ethyl* or *Othyl.*[1] At the same time he pointed out that if we could replace one atom of hydrogen in acetic acid by othyl, we should obtain a compound bearing the same relation to acetic acid as ether to alcohol—

Hydrated acetic acid.	Anhydrous acetic acid.
$\left.\begin{matrix} C_2H_3O \\ H \end{matrix}\right\}O$	$\left.\begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\right\}O$

The anhydrous acids were discovered by Gerhardt,[2] who subsequently called them *anhydrides.*[3] He obtained them by a reaction similar to that by which Williamson prepared the ethers.

Chemists now endeavoured to find among the more

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[1] *Quart. Journ. Chem. Soc.* 4, 229, 351.

[2] *Ann. Chem. Pharm.* 87, 84, and 149.

[3] *Traité*, 4, 672.

simple inorganic compounds other types for organic compounds, and thus arose Gerhardt's system of types. According to this the organic compounds of known constitution can be classed under the four types—*hydrogen, hydrochloric acid, water,* and *ammonia,* as the following examples will show—

Hydrogen.	Hydrochloric Acid.	Water.	Ammonia.
$\left.\begin{array}{r}H\\H\end{array}\right\}$	$\left.\begin{array}{r}H\\Cl\end{array}\right\}$	$\left.\begin{array}{r}H\\H\end{array}\right\}O$	$\left.\begin{array}{r}H\\H\\H\end{array}\right\}N$
Ethyl hydride. $\left.\begin{array}{r}C_2H_5\\H\end{array}\right\}$	Ethyl chloride. $\left.\begin{array}{r}C_2H_5\\Cl\end{array}\right\}$	Ethyl alcohol. $\left.\begin{array}{r}C_2H_5\\H\end{array}\right\}O$	Ethylamine. $\left.\begin{array}{r}C_2H_5\\H\\H\end{array}\right\}N$
Diethyl. $\left.\begin{array}{r}C_2H_5\\C_2H_5\end{array}\right\}$	Acetyl chloride. $\left.\begin{array}{r}C_2H_3O\\Cl\end{array}\right\}$	Ethyl ether. $\left.\begin{array}{r}C_2H_5\\C_2H_5\end{array}\right\}O$	Diethylamine. $\left.\begin{array}{r}C_2H_5\\C_2H_5\\H\end{array}\right\}N$
Acetyl hydride (Aldehyde). $\left.\begin{array}{r}C_2H_3O\\H\end{array}\right\}$	Benzoyl chloride. $\left.\begin{array}{r}C_7H_5O\\Cl\end{array}\right\}$	Acetic acid. $\left.\begin{array}{r}C_2H_3O\\H\end{array}\right\}O$	Triethylamine. $\left.\begin{array}{r}C_2H_5\\C_2H_5\\C_2H_5\end{array}\right\}N$
Acetyl-methyl (Acetone). $\left.\begin{array}{r}C_2H_3O\\CH_3\end{array}\right\}$	Cyanogen chloride. $\left.\begin{array}{r}CN\\Cl\end{array}\right\}$	Acetic anhydride. $\left.\begin{array}{r}C_2H_3O\\C_2H_3O\end{array}\right\}O$	Acetamide. $\left.\begin{array}{r}C_2H_3O\\H\\H\end{array}\right\}N$

To the first type, therefore, belong the hydrocarbons, the aldehydes, and the acetones or ketones, and to the second, besides the chlorides, the bromides, iodides, and fluorides, while the third includes not only the alcohols, ethers, monobasic acids, and anhydrides, but also the hydrosulphides, and sulphides, or those sulphur-compounds, which can be regarded as being derived from an alcohol, etc., by sulphur replacing the extra-radical oxygen. In the ammonia type were placed not only the amines, but also those compounds of phosphorus and arsenic which have a constitution analogous to that of the compound ammonias.

The next step forward was the introduction of condensed types. In the paper already referred to, Williamson pointed out that bibasic acids, such as sulphuric acid and oxalic acid, might be regarded as being derived from two molecules of water, the acid radical replacing one atom of hydrogen in each molecule at the same time. In 1854 he showed that on heating chloroform, $CHCl_3$, with sodium ethylate, $NaO\ C_2H_5$ a compound which he called tribasic formic ether, $CH(OC_2H_5)_3$, was obtained, and that this might be referred to the triply-condensed water type, just as chloroform to the triple hydrochloric acid type. These views were further developed by Odling, who extended them to a large number of compounds.[1] Thus the following formulæ were arrived at:—

Type.	Acetic acid.	Nitric acid.
$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$	$\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O$

Type.	Oxalic acid.	Tartaric acid.	Sulphuric acid.
$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}C_2O_2\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}C_4H_4O_4\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2$

Type.	Tribasic formic ether.	Citric acid.	Phosphoric acid.
$\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3$	$\left.\begin{matrix}CH\\(C_2H_5)_3\end{matrix}\right\}O_3$	$\left.\begin{matrix}C_6H_5O_4\\H_3\end{matrix}\right\}O_3$	$\left.\begin{matrix}PO\\H_3\end{matrix}\right\}O_3$

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[1] *Quart. Journ. Chem. Soc.* 7, 1.

Gerhardt adopted these views in his Treatise, though not conceiving them strictly in Williamson's sense. The theory of condensed types soon found a powerful support in Berthelot's researches on glycerin, first interpreted correctly by Wurtz, who by his brilliant discoveries of the glycols and other compounds, as well as by his ingenious speculations, became one of the chief promoters of the theory of types.

We must now proceed to examine how, mainly through the work of Kekulé, the theory of types gave rise to the conception of valency.[1]

Besides condensed types *mixed types* also came into use, such as the hydrochloric acid-water type to which Williamson's chlorhydrated sulphuric acid (chlorsulphonic acid) belongs—

$$\begin{array}{l}\left.\begin{array}{r}\mathrm{Cl}\\ \mathrm{H}\end{array}\right\}\\ \left.\begin{array}{r}\mathrm{H}\\ \mathrm{H}\end{array}\right\}\mathrm{O}\end{array}\qquad\qquad\begin{array}{l}\left.\begin{array}{r}\mathrm{Cl}\\ \mathrm{SO_2}\end{array}\right\}\\ \left.\begin{array}{r}\mathrm{H}\end{array}\right\}\mathrm{O}\end{array}$$

As Kekulé pointed out, such a fusion of several types to a condensed or mixed type can only take place by a polyatomic radical replacing more than one atom of hydrogen.[2] He says:—

"A *monatomic* radical can, therefore, never keep together two molecules of the types."

"A *diatomic* radical can unite two molecules of the types."

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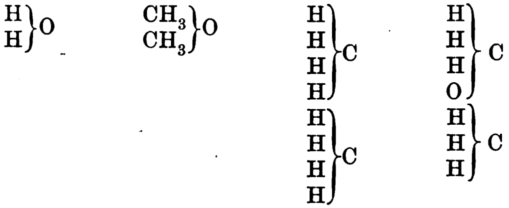
[1] "Ueber die sogenannten gepaarten Verbindungen und die Theorie der mehratomigen Radicale" (*Ann. Chem. Pharm.* 104, 129; *Lehrb.* 1, 114).

[2] As such a replacement of more than one atom of hydrogen was first observed in the case of polybasic acids, the term polybasic radicals was also used.

"A *triatomic* radical unites in the same way three molecules of the types," etc.

In the same way he distinguished monatomic, diatomic, and triatomic elements..

To Gerhardt's types Kekulé added the marsh-gas type, which is derived from tetratomic carbon. It must be distinctly pointed out that by the use of typical formulæ, it was not intended to express the position or the arrangement of the atoms in a molecule; they did not represent constitutional formulæ, but were only formulæ of decomposition, used by common consent to express a certain number of reactions. One and the same compound could, therefore, be represented by various types. Thus, for instance, methyl ether, which, according to Williamson, belonged to the water type, might also be referred to the double marsh-gas type, by assuming that it consisted of two residues of marsh gas kept together by one atom of oxygen—



$$\left.\begin{matrix}H\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}O \qquad \begin{matrix}\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}C\\ \left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}C\end{matrix} \qquad \begin{matrix}\left.\begin{matrix}H\\H\\H\\O\end{matrix}\right\}C\\ \left.\begin{matrix}H\\H\\H\end{matrix}\right\}C\end{matrix}$$

By replacing one atom of hydrogen in ammonia by methyl, we obtain methylamine, belonging to the ammonia type; but it may also be looked upon as marsh gas in which one atom of hydrogen is replaced by amide; or we may refer it to the hydrogen type and regard it as a compound of methyl with amide—

$$\left.\begin{matrix}CH_3\\H\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}H_2N\\H\\H\\H\end{matrix}\right\}C \qquad \left.\begin{matrix}CH_3\\NH_2\end{matrix}\right\}$$

Olefiant gas combines with bromine to form ethylene dibromide; in this the bromine can be replaced by hydroxyl when ethylene glycol is formed. These compounds may be represented typically by the following formulæ:—

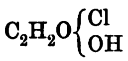
Ethylene dibromide .	$\left.\begin{matrix}C_2H_4\\Br_2\end{matrix}\right\}$	$C_2H_4\left\{\begin{matrix}Br\\Br\end{matrix}\right.$
Ethylene glycol . .	$\left.\begin{matrix}C_2H_4\\H_2\end{matrix}\right\}O_2$	$C_2H_4\left\{\begin{matrix}OH\\OH\end{matrix}\right.$

By the action of hydrochloric acid on ethylene glycol, one hydroxyl is replaced by chlorine and ethylene chlorhydrate is formed; this on oxidation yields chloracetic acid. Hence it may be regarded as chlorethyl alcohol, belonging to the water-type. But we can refer it also to mixed type water-hydrochloric acid or finally look upon it as a compound of ethylene with chlorine and hydroxyl—

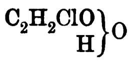
$$\left.\begin{matrix}C_2H_4Cl\\H\end{matrix}\right\}O \qquad \begin{matrix}\left.\begin{matrix}Cl\\C_2H_4\end{matrix}\right\}\\\left.\begin{matrix}\\H\end{matrix}\right\}O\end{matrix} \qquad C_2H_4\left\{\begin{matrix}Cl\\OH\end{matrix}\right.$$

Ammonia converts chloracetic acid into the monobasic amido-acetic acid, which at the same time behaves in certain relations like a compound ammonia, just as chloracetic acid presents certain analogies with ethyl chloride. Hence the formulæ of these bodies may be written in different ways—

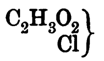
Chloracetic acid.



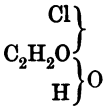
$$C_2H_2O\left\{\begin{matrix}Cl\\OH\end{matrix}\right.$$



$$\left.\begin{matrix}C_2H_2ClO\\H\end{matrix}\right\}O$$

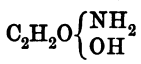


$$\left.\begin{matrix}C_2H_3O_2\\Cl\end{matrix}\right\}$$

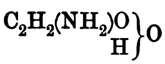


$$\begin{array}{r}Cl\\C_2H_2O\\H\end{array}\begin{array}{l}\}\\ \\ \}O\end{array}$$

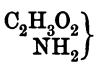
Amido-acetic acid.



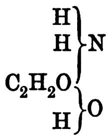
$$C_2H_2O\left\{\begin{matrix}NH_2\\OH\end{matrix}\right.$$



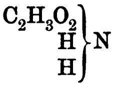
$$\left.\begin{matrix}C_2H_2(NH_2)O\\H\end{matrix}\right\}O$$



$$\left.\begin{matrix}C_2H_3O_2\\NH_2\end{matrix}\right\}$$



$$\begin{array}{r}H\\H\\C_2H_2O\\H\end{array}\begin{array}{l}\}N\\ \\ \\ \}O\end{array}$$



$$\left.\begin{matrix}C_2H_3O_2\\H\\H\end{matrix}\right\}N$$

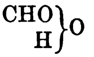
The first of these formulæ of the two compounds point out that they contain the diatomic radical C_2H_2O, the two following that they are substitution products of acetic acid, and may, like this compound, be regarded as compounds of monatomic radicals. We see further that chloracetic acid can be represented on the type water-hydrochloric acid, just as amido-acetic acid on that of water-ammonia, and finally the latter may be regarded as a compound ammonia.

Which of these formulæ is to be preferred depends upon which of the relations of the compounds it is desired to emphasise. Usually those are chosen by which the more important reactions are most simply represented.

In the year 1839 Gerhardt's attention was directed to a series of compounds formed by the action of acids on various organic substances. The acids did not simply unite with the substances as with the alkaloids to form salts, but the new compounds formed were very varied in their properties, and did not show the characteristics of their components. Water was eliminated during their formation, and under the influence of certain reagents they could reabsorb water and regenerate the acids and organic substances from which they had been prepared. To such compounds (which we now recognise as comprising the ethereal salts or esters) Gerhardt gave the name of coupled compounds (*sels copulés*); to the act of formation he applied the word *coupling* (*accouplement*). Berzelius, who in his *Jahresbericht* commented satirically upon these views, himself adopted the term *copula* in the following year, but he understood by the term something different from Gerhardt. According to Berzelius a copula was a group of atoms which acted as a kind of link between the proximate constituents of organic compounds.

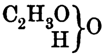
Gerhardt subsequently developed his theory of coupled compounds and modified it in different directions. It appears unnecessary to enter more closely into the history of this subject.[1] We have only to point out the conception of coupled compounds led to that of *coupled radicals*, that is, radicals which could be resolved into more simple ones, such as the radicals of the following monobasic acids :—

Formic acid.



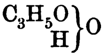
$$\left.\begin{matrix}CHO\\H\end{matrix}\right\}O$$

Acetic acid.



$$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$$

Propionic acid.



$$\left.\begin{matrix}C_3H_5O\\H\end{matrix}\right\}O$$

These compounds undergo, under certain conditions, an analogous decomposition, their radicals being

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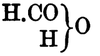
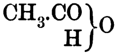
[1] Details will be found in Kekulé's *Lehrbuch*, 1, 192, and Ladenburg's *Entwickelungsgeschichte der Chemie*, 2nd ed. pp. 196 and 241.

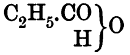
resolved into carbonyl, CO, and into hydrogen or an alcohol radical. They contain, therefore, as a proximate constituent carbonyl, which is coupled to hydrogen or an alcohol radical. This is expressed by the following formulæ:—



$$\left.\begin{matrix}H.CO\\ H\end{matrix}\right\}O$$



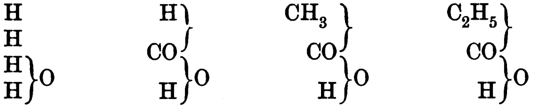
$$\left.\begin{matrix}CH_3.CO\\ H\end{matrix}\right\}O$$



$$\left.\begin{matrix}C_2H_5.CO\\ H\end{matrix}\right\}O$$

On the introduction of mixed types these acids, as well as other compounds containing coupled radicals, were referred to them as follows:—

Type. Formic acid. Acetic acid. Propionic acid.



$$\begin{array}{cccc}\text{Type.} & \text{Formic acid.} & \text{Acetic acid.} & \text{Propionic acid.}\\ \begin{matrix}H\\ H\\ \left.\begin{matrix}H\\ H\end{matrix}\right\}O\end{matrix} & \begin{matrix}\left.\begin{matrix}H\\ CO\end{matrix}\right\}\\ \left.\begin{matrix}\\ H\end{matrix}\right\}O\end{matrix} & \begin{matrix}\left.\begin{matrix}CH_3\\ CO\end{matrix}\right\}\\ \left.\begin{matrix}\\ H\end{matrix}\right\}O\end{matrix} & \begin{matrix}\left.\begin{matrix}C_2H_5\\ CO\end{matrix}\right\}\\ \left.\begin{matrix}\\ H\end{matrix}\right\}O\end{matrix}\end{array}$$

The followers of Berzelius, of whom Kolbe and Frankland were the most distinguished, held similar views, but not accepting at that time either the new atomic weights or the existence of radicals containing oxygen, they employed other formulæ. Thus Kolbe regarded acetic acid as the hydrate of the trioxide of a radical consisting of methyl coupled to carbon, and he wrote its formula $HO(C_2H_3)C_2O_3$.

The extension which Kekulé gave to the theory by the introduction of mixed types soon brought about the dissolution of Gerhardt's too limited types. "Gerhardt's types rendered great service in the development of the science, but they can only be regarded as a part of the scaffolding, which was removed when the erection of the system of organic chemistry had made sufficient progress to be able to dispense with it. The comparison of a large number of compounds with a small number of types afforded numberless opportunities of reviewing individual cases in a variety of ways; cases of analogy and of contrast thus became apparent, and finally a general survey of the remarkable behaviour of the chemical atoms in compounds was acquired."[1]

By going back from the radicals to the atoms the foundation of our present theory, which surpasses all previous ones by its surprising simplicity, was laid. Kekulé first insisted upon the necessity of this step.[2] Some time later Couper showed even more pointedly that only by going back to the atoms should we be enabled to ascertain the manner in which they attract each other in a molecule.[3]

An attempt towards this had already been made by Frankland in 1852, when he said: "When the formulæ of inorganic chemical compounds are considered, even a superficial observer is impressed with the general symmetry of their construction. The compounds of nitrogen, phosphorus, and arsenic, especially, exhibit the tendency of these elements to form compounds containing 3 or 5 atoms of other elements; and it is in these proportions that their affinities are best satisfied; thus in the ternal group we have NO_3, NH_3, NI_3, NS_3, and in the five-atom group, NO_5, NH_4O, NH_4I, PO_5, PH_4I, etc. Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, *it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that, no matter what the character of*

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[1] Lothar Meyer's *Modern Theories*, translated by Bedson and Williams, p. 194.

[2] *Ann. Chem. Pharm.* 104, 129.

[3] *Ibid.* 110, 46; *Phil. Mag.* (4), 16, 104.

the uniting atoms may be, the combining power of the attracting element, if I may be allowed the term, is always satisfied by the same number of atoms. It was probably a glimpse of an operation of this law amongst the more complex organic groups which led Laurent and Dumas to the enunciation of the theory of types; and had not these distinguished chemists extended their views beyond the point to which they were well supported by then existing facts, had they not assumed that the properties of an organic compound are dependent upon the *position* and not upon the *nature* of its single atoms, that theory would have undoubtedly contributed to the development of the science to a still greater extent than it has already done."[1]

More recently Frankland has pointed out that, "This hypothesis constitutes the basis of what has since been called the doctrine of atomicity or the equivalence of elements; and it was, so far as I am aware, the first announcement of this doctrine."[2]

It was not only this; it was more. We find here an opinion pronounced which afterwards led to a most interesting controversy, *i.e.* whether the atomicity of an element is constant or variable. The doctrine of constant valency was held by the chemists of Gerhardt's school, of which Kekulé is the chief representative, and it is indeed easy to see that the theory of types must have led to the conception of a constant atom-fixing power.

The typical elements or those which keep the molecule together were, as already mentioned, first distinguished as being *monobasic* and *polybasic* or

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[1] *Ann. Chem. Pharm.* 85, 368; *Phil. Trans.* 142, 417.

[2] *Experimental Researches*, 1877, 145.

monatomic and *polyatomic.*[1] These terms were, however, soon found to be very inappropriate, inasmuch as we cannot well speak of a monatomic or a diatomic atom; and again the terms monobasic and polyatomic remind us that the doctrine of a multiple saturating power issued from Liebig's investigation of the polybasic acids, and cannot, therefore, be applied to the atoms. Erlenmeyer, therefore, proposed the terms *ein- zwei- drei-* and *vierwerthig,*[2] which have come into general use in Germany; while L. Meyer's proposal to use the words *univalent, bivalent, trivalent,* and *quadrivalent*[3] has been adopted in France.[4] Atomicity was changed first into *quantivalence* and then into *valency* or *chemischer Werth.*

In England we use the terms *monad, dyad, triad,* and *tetrad,* which Odling first proposed.[5] The two first of these were first employed by Laurent, but in a quite different sense. He called the bivalent and quadrivalent elements *monads,* because a single atom of them may be added to a compound as in the conversion of aldehyde, C_2H_4O, into acetic acid, $C_2H_4O_2$; while the univalent and trivalent elements were *dyads,* because they can be added in pairs only, as in the formation

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[1] The terms monatomic and polyatomic had been used much earlier but in a different sense. Thus Berzelius, in 1827, called fluorine, chlorine, etc., *polyatomic,* because several atoms of them unite with a single atom of another element. Gaudin de Saintes employed the same terms in 1833 in the sense in which they ought to be and have been since used by Gmelin, Clausius, and Odling, *i.e.* to express the number of atoms in a molecule. Thus mercury forms a monatomic, oxygen a diatomic, and water a triatomic gas (see L. Meyer, *loc. cit.* 181).

[2] *Zeitsch. Chem.* 1860, 540.

[3] L. Meyer, *Moderne Theorien,* 1st ed. 1864, 76.

[4] Wurtz, *La Théorie Atomique,* 187.

[5] *Tables of Chem. Form.* 1864.

of ethylene dichloride, $C_2H_4Cl_2$, from olefiant gas, C_2H_4.[1]

In order to avoid confusion, Odling proposed to call the former *Artiads* (ἄρτιος, even), and the latter *Perissads* (περισσός, uneven), but this proposal never came into general use.[2]

We cannot here discuss the interesting question whether the quantivalence of an element is constant or variable, and must refer our readers who take an interest in this subject to Lothar Meyer's *Modern Theories.*

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[1] *Chemical Method*, 47.

[2] *Phil. Mag.* Feb. 1864.

V

Compound radicals exist in inorganic compounds as well as in organic substances — All organic compounds contain carbon — This element differs from all other elements qualitatively and quantitatively—Organic chemistry is the chemistry of the hydrocarbons and their derivatives—Homologous series.

WE must interrupt our narrative once more. Liebig had defined organic chemistry as the chemistry of compound radicals. Williamson and Odling, however, in applying the theory of types to inorganic compounds, showed that these also contain compound radicals. It is true the existence of these had been assumed, but their number was limited to ammonium, NH_4, cyanogen, CN, and uranyl, UO_2. Now, however, they became so numerous that Liebig's definition could no longer be maintained.

The only difference remaining between the two divisions of chemistry was, as it had been at the time of Stahl and of Lavoisier, a qualitative one. All compounds formed in organic nature contain carbon and hydrogen, the majority also oxygen, and many, in addition to these, nitrogen. In accordance with older views it was still believed by many that the hydrogen in several cases existed in the form of water, as in oxalic acid, and consequently the only element common to all organic compounds was carbon, as Gerhardt had pointed out in 1846.

Organic chemistry might, therefore, have been defined as the chemistry of the carbon compounds, or of compound radicals containing carbon. But by such a definition several compounds of this element which are not formed in the organism, such as carbonic oxide, carbon oxychloride, carbon disulphide, and the chlorides of carbon, or others which chiefly occur in the mineral kingdom, such as marsh gas and carbon dioxide, would have been included among organic bodies. Such a consequence being shunned, attempts were made to get over this difficulty in several ways.

Gmelin, who used the equivalent weights, believed that he had found a boundary-line, and wrote, in 1848 :

" Organic compounds do not by any means differ from those of the inorganic kingdom in the elements of which they are composed. The elements by which the former are produced are likewise found in the latter; but while all the elements can combine to form inorganic compounds, only a limited number of them are capable of entering into compounds of the organic class. All organic compounds contain carbon ; most of them contain hydrogen and oxygen; a few nitrogen; and a very few contain phosphorus, sulphur, iodine, bromine, chlorine, etc. From this small number of elements there are formed several thousands of organic compounds, distinguished from one another, either by the different nature and relative quantities of their constituents, or, when the composition is the same, by isomeric, metameric, and polymeric relations.

" *Carbon* is the only element which is essential to organic compounds. Every one of the other elements may be absent from particular compounds; but no compound, which in all its relations deserves the name of organic, is destitute of carbon.

"If we were to regard as organic, those carbon compounds which have hitherto been classed among inorganic substances, viz. carbonic oxide, carbonic acid, sulphide of carbon, phosgene, cast-iron, etc. we might define *Organic Compounds* simply as the *Compounds of Carbon.*

"But organic compounds are still further distinguished by containing more than one atom of carbon."

He adds that we are often led to this supposition by observing the proportions in which the elements are combined. Thus cyanogen contains 14 parts of nitrogen to 12 parts of carbon; hence its formula is C_2N. In other compounds the same conclusion is deduced from the proportion in which they combine with other substances. Thus the most simple formula of acetic acid is CHO; but as one equivalent of potash requires for neutralisation a quantity of acetic acid corresponding to the formula $C_4H_4O_4$, we must adopt the latter.

He continues: "Hence *Organic Compounds* are all *Primary Compounds containing more than one atom of carbon.*"[1] By primary compounds he meant such as cannot, like bicarbonate of potash (at that time regarded as a compound of K_2CO_3 and H_2CO_3), be formed by the simple additive combination of other compounds.

This definition consequently excluded the oxides, the sulphide, the oxychloride of carbon, etc., while it included marsh gas, methyl alcohol, and formic acid.

[1] Gmelin's *Handbook Org. Chem.* i. 4.

But when Gerhardt's atomic weights had been universally recognised, and it was found that the oxides of carbon, etc. contain the same quantity of carbon in a molecule as the most simple organic compounds, Gmelin's definition could be no longer maintained, unless, indeed, either the latter were regarded as inorganic bodies or the former as organic ones. The second alternative was preferred.

In 1851 Kekulé wrote as follows: "We have now come to the conviction that the chemical compounds found in the vegetable and animal kingdoms contain the same elements as the bodies existing in inanimate nature. We are convinced that in the one the elements obey the same laws as in the other, and consequently that no difference exists between inorganic and organic compounds with regard to either the matter or the forces concerned, or the number and the arrangement of the atoms. We observe a continuous series of compounds, the single members (comparing only those which are placed near together) resembling each other so closely that no natural boundary can be traced anywhere. But if we want to make one, which indeed we must do for the sake of clearness, such a boundary is not a natural one, but is quite arbitrary, and therefore we may draw that boundary line where-ever we find it convenient. If we retain the old division, it appears most convenient to place, as has already been done, all compounds of carbon together, and describe them in the part called organic chemistry.

"We define, therefore, *Organic Chemistry as the Chemistry of the Carbon Compounds.* But this does not imply any real difference between inorganic and organic bodies. That part of our science to which the time-honoured name *Organic Chemistry* is given, and which we more conveniently call the *Chemistry of the Carbon Compounds,* is only a special part of *pure chemistry* treated separately, the large number and importance of the carbon compounds rendering such a special study of them necessary."[1]

Other chemists expressed similar views. Erlenmeyer says that a division of labour is requisite in the interest of teaching. "Besides," he adds, "it cannot be denied that by reason of certain properties possessed by carbon, the compounds of this element exhibit certain peculiarities in their chemical behaviour. Their study, therefore, requires in many respects peculiar methods of investigation, different from those employed in the study of the compounds of other elements; and thus the necessity for a division of labour has also made itself apparent in the interest of scientific research."[2]

Butlerow is also of opinion that organic chemistry must be defined as the *chemistry of the carbon compounds.* "These compounds must, without doubt, be treated generally in their proper place in the system; but their large number, the peculiarity of their chemical character, and their importance, necessitate their description in a separate part,—a partition, which if somewhat unnatural and not quite correct, is at least very convenient."[3]

Such a separation, however, has nowhere been consistently carried out. No chemist ever thought of omitting the oxides of carbon, its sulphide, etc., from the inorganic division, much less of placing soda-ash,

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[1] Kekulé, *Lehrb.* 1, 10.

[2] Erlenmeyer, *Lehrb.* 1, 5.

[3] Butlerow, *Lehrb.* 5.

calcspar, spathose iron-ore and similar carbonates, or cast-iron among the organic compounds.

When it was stated that organic compounds exhibited certain peculiarities which distinguished them from compounds occurring in the mineral kingdom, no great advance had been made on the standpoint of Gmelin, who said in 1817 that the difference could be better felt than defined. On looking over modern books on chemistry we find that the oxides of carbon, its sulphide, and a number of their derivatives, are described in the inorganic, as well as in the organic part, or some of them in the former, and others in the latter part. The same is the case with the cyanogen compounds, the simple reason being that these bodies, containing only one atom of carbon in the molecule, bear in many respects great resemblance to the compounds of the other elements. On the other hand, wood spirit and formic acid, which also contain one atom of carbon in the molecule, have never been regarded as inorganic compounds, because they show the closest relationship to spirit of wine, acetic acid, and analogous compounds, with more than one atom of carbon. Indeed, it was the peculiar behaviour of the latter bodies which led to the division of pure chemistry into two parts. The cause of this peculiarity is not far to seek. Carbon possesses certain characteristic properties by which it differs from all the other elements.

First of all the number of its compounds is larger than those of all the other elements taken together, and although those produced by organic life consist only of a few elements, the number of atoms forming a molecule is frequently very large, as the following examples show :—

Oil of Turpentine	$C_{10}H_{16}$
Cane sugar	$C_{12}H_{22}O_{11}$
Stearin	$C_{57}H_{110}O_6$
Albumin [1]	$C_{210}H_{330}N_{52}O_{66}S_3$
Starch [2]	$C_{1200}H_{2000}O_{1000}$

In order to explain the existence of such a large number of carbon compounds, we must assume with Kekulé and Couper that the carbon atoms possess the property of combining with each other, a point to be discussed farther on. The atoms of other polyvalent elements possess this property too, but only to a limited extent. In the case of carbon no limit has yet been found. *A large number of its atoms can unite, forming a group which in many reactions behaves as a chemical whole.*

But carbon differs from all other elements by the property *that in such a group all the free combining units can be saturated by hydrogen.*

We are, therefore, acquainted with a large number of hydrocarbons, a number increased almost daily by the discovery of new ones. All of them are volatile, whilst among the other elements only those of the chlorine group, oxygen group, nitrogen group, as well as boron and silicon, form volatile hydrides, and in no case are more than three hydrides known.

The hydrocarbons are not only the most simple carbon compounds, but also, from a theoretical point of view, are the most important, because all other carbon compounds are derived from them by the substitution of other elements for hydrogen. In those carbon compounds found in nature a part of the hydrogen is

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[1] Harnack, *Ber. deutsch. chem. Ges.* 23, 40.

[2] Brown and Morris, *Journ. Chem. Soc.* 1889, 1, 465.

generally replaced by oxygen, nitrogen, or by both, and a few also contain sulphur. All the other elements can, however, be introduced artificially into carbon compounds, but there are only a few cases in which all the hydrogen can be replaced. The number of chlorides of carbon is, therefore, much smaller than that of the hydrocarbons. With oxygen carbon forms only two compounds, and with nitrogen it combines only in one proportion. Consequently the majority of its compounds contain hydrogen, or a residue of the hydrocarbon, from which they are theoretically derived.

We define, therefore, that part of our science which is commonly called organic chemistry as the *Chemistry of the Hydrocarbons and their Derivatives.*[1]

The correctness of this definition is proved by the fact that, as soon as the chemical constitution of a carbon compound is clearly understood, we can convert it into the corresponding hydrocarbon, or obtain it from the latter. The most striking example relates to the discovery of artificial alizarin, which will be described later.

But even this definition does not fix a sharp boundary-line between inorganic and organic chemistry, for the compounds containing one atom of carbon, such as carbon dioxide, carbon oxychloride, carbon disulphide, prussic acid, etc., which are commonly described in the inorganic part, are as much derivatives of marsh gas, CH_4, the most simple hydrocarbon, as methyl alcohol and formic acid.

If we burn this gas in the air, water and carbon dioxide are produced, monad hydrogen being replaced by dyad oxygen. Marsh gas cannot be converted into carbon disulphide, but we can obtain the former from

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[1] Schorlemmer, *Carbon Compounds*, 6.

the latter by passing its vapour, mixed with hydrogen sulphide, over red-hot copper—

$$CS_2 + 2SH_2 + 8Cu = CH_4 + 4Cu_2S$$

When we act on marsh gas with chlorine, we obtain methyl chloride as the first substitution product—

$$CH_4 + Cl_2 = CH_3Cl + HCl$$

On heating this with caustic potash it is converted into wood spirit or methyl alcohol—

$$CH_3Cl + KOH = CH_3.OH + KCl$$

On oxidation this compound yields formic acid, CH_2O_2, two atoms of hydrogen being exchanged for one of oxygen.

By the further action of chlorine on marsh gas or methane, we obtain methylene chloride, CH_2Cl_2, trichlormethane or chloroform, $CHCl_3$, and finally tetrachlormethane, CCl_4. If we heat chloroform with ammonia it is converted into hydrocyanic acid, three atoms of chlorine being replaced by one atom of nitrogen—

$$CHCl_3 + 4NH_3 = CHN + 3NH_4Cl$$

Now, as all cyanides are derived from hydrocyanic acid, we must regard these as derivatives of marsh gas, and likewise all carbonates, for an aqueous solution of carbon dioxide contains carbonic acid, $CO(OH)_2$, *i.e.* marsh gas, in which one-half of the hydrogen is replaced by oxygen, and the other half by hydroxyl.

Even the different kinds of cast-iron, or rather the different kinds of iron carbides contained in it, must be regarded as derivatives of hydrocarbons, for such compounds are formed on dissolving the metal in hydrochloric or in dilute sulphuric acid, the metal being exchanged for hydrogen.

Only one carbon compound exists, of which the corresponding hydrocarbon is not known. This is the most simple of all, carbonic oxide, CO. All attempts made to obtain the hydrocarbon methylene, CH_2, have failed, and we have reason to suppose that this compound is not capable of existence.

Marsh gas is the only hydrocarbon containing one atom of carbon in a molecule, but we know three with two atoms of carbon—

Ethane, C_2H_6, Ethylene, C_2H_4, Acetylene, C_2H_2

In order to explain their constitution, we assume that in ethane the carbon atoms are linked together by one combining unit of each, in ethylene or ethene by two, and in acetylene or ethine by three; in other words, that the two carbon atoms of ethane form a hexad, in ethene a tetrad, and in ethine a dyad group. In a similar manner three and more carbon atoms may be linked together. The above form the initial members of groups or series in which each member differs from the preceding one by containing one atom of carbon and two atoms of hydrogen more.

When Laurent in 1836 brought forward his nucleus theory, he arranged organic compounds in series, but J. Schiel first pointed out, in 1842, that the radicals of the bodies commonly called alcohols, formed not only a most simple and regular series, but that their properties also exhibited a corresponding regularity. He used of course the equivalent weights, and calling the hydrocarbon compound $C_2H_2 = R$, wrote—

R_1H = Methyl
R_2H = Ethyl
R_3H = Glyceryl
R_4H = ?
R_5H = Amyl
$R_{16}H$ = Cetyl
$R_{24}H$ = Cerosyl

He was of opinion that other similar series existed.[1] Soon after, Dumas showed that the fatty acids formed such a series: "If we start from margaric acid, $C_{34}H_{68}O_4$, so well investigated by Chevreul, and subtract equivalents of carbon and hydrogen, we obtain a series of seventeen acids, of which at least nine are known. This series contains the principal fatty acids. It knits margaric acid by quite unsuspected threads, to formic acid standing apparently the most distant from it."[2]

While Schiel pointed out that in the case of the alcohols the boiling point increases as we ascend the series, Dumas showed that in a similar way the melting point of the fatty acids rises.

Gerhardt in 1843, and in his *Précis de Chimie Organique*, 1844 and 1845, thereupon arranged a large number of compounds in such series, which he called *homologous*. Bodies such as ethyl alcohol, ethyl chloride, ethyl-amine, acetic acid, which are produced from each other by simple chemical reactions, were named *heterologous* compounds.

Such a classification into homologous and hetero-

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[1] *Ann. Chem. Pharm.* 43, 107.
[2] *Ibid.* 45, 330.

logous series he compared to a pack of cards arranged in such a way that all cards of the same value are placed in the same horizontal row, and those of the same suit in the same vertical row. The former correspond to the homologous and the latter to the heterologous series. If a card is missing we know its place, its suit, and its value. The same holds good for homologous compounds; if the series is incomplete, we not only know the composition of the missing members and their principal properties, but we also can find means of preparing them if we want to complete the series.

From the hydrocarbons above mentioned the following homologous series are derived:—

C_nH_{2n+2}		C_nH_{2n}		C_nH_{n-2}	
Methane	CH_4	...		...	
Ethane	C_2H_6	Ethene	C_2H_4	Ethine	C_2H_2
Propane	C_3H_8	Propene	C_3H_6	Propine	C_3H_4
Butane	C_4H_{10}	Butene	C_4H_8	Butine	C_4H_6
Pentane	C_5H_{12}	Pentene	C_5H_{10}	Pentine	C_5H_8
Hexane	C_6H_{14}	Hexene	C_6H_{12}	Hexine	C_6H_{10}
etc.		etc.		etc.	

This nomenclature, which was proposed by Hofmann, has not been strictly practised, owing chiefly to ambiguity arising from the pronunciation of the terminal syllables. Thus for ethene, propene, etc., we generally use the older names ethylene, proplyene, etc.; ethine is better known as acetylene, etc.

The members of the first series have been called *saturated hydrocarbons* or the "limit hydrocarbons" (*Grenzkohlenwasserstoffe*), as no hydrocarbon can exist containing more hydrogen than is expressed by the general formula of this group. The highest members are solids at the common temperature; they were discovered in 1830 by Reichenbach, who found them in wood tar, and as they are not attacked by concentrated nitric acid, or other powerful chemical agents, he called them—believing the mixture to be a definite compound—*paraffin* (derived from *parum affinis*), in order to designate "its most striking property, its few and weak affinities." As the lower members behave in the same way, Henry Watts proposed to call the whole series the *paraffins*, and this name has been accepted.

The second series we call, with Guthrie, the *Olefines*, after the initial member, which was first known as olefiant gas.

Besides these three series others are known such as C_nH_{2n-4}, C_nH_{2n-6}, etc.; the initial members obviously containing more than two atoms of carbon.

From these hydrocarbons a very large number of other compounds are derived. Just as by the action of chlorine on marsh gas we obtain methyl chloride we can, in like manner, obtain from the higher paraffins chlorides of monad radicals, having the general formula $C_nH_{2n+1}Cl$. The chlorine of these can be replaced by hydroxyl, a series of hydroxides, $C_nH_{2n+1}OH$, being obtained, which we call the *alcohols*.[1]

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[1] The name alcohol was first given to spirits of wine or ethyl alcohol, and then used as a generic term for the whole group. In Hebrew and Arabic *kohl* is the name of native antimony sulphide, which, as an impalpable powder, has been used from early times, and is still used in the East for painting the eyebrows. This custom we find mentioned in Ezekiel and in the Second Book of Kings (Kopp, *Geschichte der Chemie*, iv. 100). The Spaniards, who took many words from the Arabic, translated the passage in which Ezekiel mentions it, *alcoholaste tus ojos*.

Afterwards the word alcohol became a generic term for a fine powder, and to-day powdered iron is still called in pharmacy *alcohol ferri* or *ferrum alcoholisatum*. Paracelsus uses it in the same sense, and speaks of antimony which has been changed into the alcool (*Chirurg. Schrifft.* 1618, p. 104); while mentioning the sediment of wine, which he calls *tartarus*, he says, "*Alcool id est tartarus resolutus*

When methyl chloride is heated with ammonia it is converted into methylamine—

$$CH_3Cl + NH_3 = CH_3 . NH_2 + HCl$$

By the same reaction, the other chlorides can be changed into amines of the general formula $C_nH_{2n+3}N$; and just as methyl alcohol yields formic acid by oxidation, so we can replace in all alcohols two atoms of hydrogen by one of oxygen, and thus obtain the series of the fatty acids $C_nH_{2n}O_2$.

Thus we have the following homologous and heterologous series:—

CHLORIDES.		AMINES.	
Methyl chloride	CH_3Cl	Methylamine	$CH_3.NH_2$
Ethyl chloride	C_2H_5Cl	Ethylamine	$C_2H_5.NH_2$
Propyl chloride	C_3H_7Cl	Propylamine	$C_3H_7.NH_2$
Butyl chloride	C_4H_9Cl	Butylamine	$C_4H_9.NH_2$
Amyl chloride	$C_5H_{11}Cl$	Pentylamine	$C_5H_{11}.NH_2$
Hexyl chloride	$C_6H_{13}Cl$	Hexylamine	$C_6H_{13}.NH_2$

ALCOHOLS.		FATTY ACIDS.	
Methyl alcohol	$CH_3.OH$	Formic acid	CH_2O_2
Ethyl alcohol	$C_2H_5.OH$	Acetic acid	$C_2H_4O_2$
Propyl alcohol	$C_3H_7.OH$	Propionic acid	$C_3H_6O_2$
Butyl alcohol	$C_4H_9.OH$	Butyric acid	$C_4H_8O_2$
Amyl alcohol	$C_5H_{11}.OH$	Valerianic acid	$C_5H_{10}O_2$
Hexyl alcohol	$C_6H_{13}.OH$	Caproic acid	$C_6H_{12}O_2$

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in minutas partes" (*Opera*, 1616, i. 735). At the same time he uses the term for the designation of a volatile body. Speaking of "*primum ens metallorum*," he says: "Of this Primo Ente you must understand that it is a volatile spirit, which sometimes resembles a liquor and sometimes an alcool" (*Op.* i. 906). Alcool or alcohol vini he mentions very often, and once he adds "*id est vino ardente*" (*Op.* i. 178).

His followers also use alcohol vini as a name for spirits of wine; and Quercetanus says, "*Spiritus vini alcoholisatus circulationibus*" (*Pharm-dogmat.* 1613, pp. 283, 286), showing that the strengthening of spirits of wine by rectification was also called alcoholisation.

Besides these, a large number of other derivatives are known, which can be arranged in a similar way, and the same holds good for the derivatives of the other series of hydrocarbons.

All hydrocarbons contain an even number of hydrogen atoms, in consequence of carbon being a tetrad element. It is obvious, too, *that the sum of the atoms of monad and triad elements, contained in a molecule of a carbon compound, must also be an even number.*

If we compare the properties of the members of a homologous series, as, for instance, those of the group C_nH_{2n+2}, we find that they differ from each other in their *physical properties.* The lowest members are gaseous at the ordinary temperature, the succeeding ones are liquids, their boiling point increasing with the molecular weight, and the highest members are solids, which volatilise only at a high temperature. The same holds good for other series, their initial members being gases or very volatile liquids, and the highest consisting of solids, which volatilise only with difficulty or not without more or less decomposition.

On the other hand, the *chemical character* of each series depends on the manner in which the carbon atoms are linked together or combined with other elements, and therefore the members of a homologous series exhibit a very similar chemical behaviour.

A consequence of this is that while the comparatively limited number of compounds of other elements allows us to ascertain the nature and composition of a substance by observing a few reactions, this is only exceptionally the case with carbon compounds. Only a limited number are recognisable by qualitative analysis. In most cases we are obliged to obtain the body to be examined in a pure state, to determine its physical and chemical properties, and then to ascertain its quantitative composition. Not only do newly discovered compounds require such an elaborate treatment, but very often bodies, which have been known for a long time, can only be identified in this way.

The progress of organic chemistry was, in consequence, intimately connected with that of chemical analysis.

VI

Organic analysis—Calculation of formulæ—Determination of molecular weight—Rational formulæ—Graphic formulæ.

IT has already been mentioned that Berzelius improved the older methods of organic analysis, and worked out a more exact one, which he published in 1814.[1] By its means he was enabled to prove that the organic bodies follow the same stoichiometric laws as the inorganic compounds. The process, however, contained certain sources of error which prevented a very exact determination of carbon and hydrogen.

To Liebig belongs the great merit of having perfected and simplified the operations for the ultimate analysis of organic compounds, and this to such a degree that his method has not since been subjected to any essential alterations. For six years he was fully occupied in the attempt to reach this goal, and only in 1831, when he described his potash bulbs, did his task appear to be completed.[2] He says: "It is clear that one may reach a proposed object by different ways, and that the means which are described in what follows are capable of improvement; yet all so-called

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[1] Thomson's *Ann. phil.* 4, 401.

[2] *Pogg. Ann.* 21, 1; *Handwörterbuch*, 1842, 1, 357; *Anleitung zur Analyse org. Körper, Braunschweig*, 1837.

improvements and perfections, which have hitherto been proposed, only prove want of acquaintance with the general principle of what is properly called a *method*."

"There exists in the human mind a spontaneous striving for perfection, and hence arise the efforts for perfecting what already is and for finding new ways to reach a given end. As a rule, however, a mistake of quite a general character is made—namely, we neglect to test the practicability of the means already existing or indeed to make ourselves acquainted with them. We begin by departing from the usual path, and if our efforts are crowned with success, the satisfaction of the inventive spirit leads us to overlook the detours and difficulties which had to be traversed, and which we should not have come upon had we followed the beaten track. In what follows we hold by the rule of Berzelius, the most experienced chemist of our own, and probably of all time, and of two equally good methods we prefer the simpler to the more complicated one."

Having solved his task Liebig was enabled, in conjunction with his pupils, to carry out the researches which soon made his laboratory in Giessen famous throughout the civilised world.

As an example of one of his analyses, we will take that of sugar, which had been analysed before by several chemists—

	GAY-LUSSAC AND THÉNARD.	BERZELIUS.	LIEBIG.	CALCULATED.
Carbon	41·36	42·7	41·71	42·10
Hydrogen	6·39	6·5	6·45	6·44
Oxygen	51·14	50·8	51·84	51·46
	98·89	100·0	100·00	100·00

The reason that the numbers of the three last analyses add up exactly to 100, is that the oxygen has not been directly determined but has been found by difference.

Liebig also devised new methods for the determination of nitrogen. One of these was improved by Dumas and other chemists, whilst another, which can only be employed in certain cases, but is distinguished by its simplicity and rapidity, we owe to Liebig's pupils Varrentrapp and Will.

When from the results of an analysis, we have calculated the percentage composition of a compound, we want next to find its formula. In the case of inorganic bodies this can generally be done without any difficulty, as we can easily determine the ratio of the number of atoms contained in it. Organic bodies, however, have generally a more complicated composition, and, as the following examples will show, the results of the analysis are not sufficient to establish a formula.

A volatile liquid which was obtained from petroleum gave the following results:—

Carbon . .	83·8
Hydrogen . .	16·3
	100·1

From this we see that it is a hydrocarbon, and by dividing these numbers by the atomic weights—

$$83{\cdot}8 \div 12 = 6{\cdot}98$$
$$16{\cdot}3 \div 1 = 16{\cdot}30$$

we find that the compound is a paraffin. Now as in organic analysis we generally find the carbon a little too low and the hydrogen a little too high, we might be inclined to regard the body as heptane, C_7H_{16}, although the numbers found agree better with the composition of hexane, C_6H_{14}. The possibility that it is even octane is not excluded, as these hydrocarbons contain in 100 parts—

	HEXANE.	HEPTANE.	OCTANE.
Carbon . .	83·72	84·0	84·21
Hydrogen . .	16·28	16·0	15·79
	100·00	100·0	100·00

Moreover, the substance may contain a small admixture of the homologues with which it is associated in petroleum, and therefore all that we can say is that our hydrocarbon is a paraffin, containing probably not less than six and not more than eight atoms of carbon.

In still more complicated cases we are quite at a loss to calculate a formula from the analytical data. A number of analyses of an orange colouring matter called aurin gave the following results:—

	(1)	(2)	(3)
Carbon . .	78·79	78·48	78·42
Hydrogen . .	5·00	5·06	4·89
Oxygen . .	16·21	16·46	16·69
	100·00	100·00	100·00

These numbers add up exactly to 100, because we have no simple means for a direct determination of oxygen. If we have determined all the elements occurring in a compound and find that the percentage numbers do not add up to 100, we take the difference as consisting of oxygen. Hence on subjecting a compound to ultimate analysis, we must first know which elements are present in it, or else, as has sometimes been the case, grave mistakes will be made.

A good example is found in taurin, a body first obtained by Gmelin from the bile of the ox (taurus), and analysed by Demarcay and by Pelouze and Dumas with concordant results. From these they calculated the formula $C_2H_7NO_5$, which was generally accepted, although it did not agree with the properties of the substance. It was to be expected that a body containing so much oxygen would be very unstable, whilst taurin was not attacked by concentrated sulphuric acid in the cold, and could even be boiled down with concentrated nitric acid without undergoing decomposition.

As it appeared quite improbable that a compound with 63 per cent of oxygen could be such an indifferent body, Redtenbacher examined it again in Liebig's laboratory, and found that by fusing it with potash, it was decomposed with the formation of sulphurous acid. Taurin, therefore, contains sulphur, and its formula is $C_2H_7NO_3S$.

The reason these distinguished chemists overlooked the presence of this element, was that the properties of taurin differed so much from all organic sulphur compounds then known, that nobody had the slightest suspicion of the presence of sulphur. Moreover, as it happens that the atomic weight of sulphur is exactly twice that of oxygen, a simple formula could readily be calculated.

Now, in the case of aurin, we know that it consists only of carbon, hydrogen, and oxygen. From the percentage composition, however, a number of probable formulæ can be calculated. Of these we will give only three and the percentage composition corresponding to each—

	$C_{13}H_{10}O_2$	$C_{19}H_{14}O_3$	$C_{25}H_{18}O_4$
Carbon . .	78·79	78·62	78·53
Hydrogen . .	5·05	4·83	4·71
Oxygen . .	16·16	16·55	16·76
	100·00	100·00	100·00

It is clear that analysis alone cannot lead us to the true formula. We want not only to find the most simple formula of a compound, but, if possible, its molecular formula. This is easily done if we can determine the molecular weight of the body.

Until recently the only reliable means for doing this was the determination of the vapour density, if the body could be volatilised without decomposition. From the density or specific gravity of the vapour we can easily find how many times heavier it is than hydrogen, and this number, multiplied by two, gives, according to Avogadro's law, the molecular weight.

A chemist undertaking researches in the field of organic chemistry must, therefore, be well acquainted not only with the methods of ultimate analysis but also with those for the determination of vapour density.

Until recently two methods were in use, that of Gay-Lussac, involving the determination of the volume of a given weight of vapour, and that of Dumas, in which the weight of a given volume of vapour is found. The first method could only be used in the case of very volatile bodies; while the second, though not limited in the same way, had the disadvantage of requiring larger quantities of the substance in order to drive the air out of the apparatus, a circumstance which in the case of valuable preparations had to be considered.

Chemists, therefore, looked out for improvements;

and Hofmann succeeded in improving Gay-Lussac's method to such an extent that it soon came into general use. Victor Meyer has since devised new methods, and of these, one distinguished by its simplicity and by being applicable for any temperature, is now usually employed.

If we know the composition and the vapour density of an organic compound, we can in most cases easily ascertain its molecular formula. Sometimes a decision may become doubtful. Thus two hydrocarbons, having very similar properties, gave the following numbers:—

	(a)	(b)
Carbon . .	94·1	93·8
Hydrogen . .	5·9	6·3
	100·0	100·1
Molecular Weights .	180·6	189·0

The latter quantities contain—

Carbon . .	169·4	177·3
Hydrogen . .	10·6	11·7
	180·0	189·0

On dividing these numbers by the atomic weights we have—

	(a)	(b)
Carbon atoms . .	14·1	14·7
Hydrogen atoms . .	10·6	11·7

From this it appears probable that the formula of (*a*) is $C_{14}H_{10}$, and that (*b*) is its next higher homologue $C_{15}H_{12}$, although, inasmuch as in the calculations the errors of experiment have accumulated, the numbers do not agree well with this formula. We can eliminate them again to some extent by calculating the theoretical composition and vapour density, and comparing the numbers with the experimental data—

	(a)		(b)	
	calc.	found.	calc.	found.
Carbon . .	94·38	94·1	93·75	93·8
Hydrogen . .	5·62	5·9	6·25	6·3
	100·00	100·0	100·00	100·1
Mol. weight .	178	180	192	189

The numbers obtained by experiment agree with those required by theory within the limits of unavoidable errors, and quite closely enough to justify us in accepting the above formulæ for the hydrocarbons, which, as their further investigation proved, were anthracene, $C_{14}H_{10}$, and methylanthracene, $C_{14}H_9 . CH_3$.

In a few cases the determination of the vapour density is quite sufficient to give the molecular formula of a body. All that is required is to know that it belongs to a definite series and to have it in a state of purity, as is indicated by a constant boiling point. Thus we can easily recognise a paraffin by its resistance to cold concentrated sulphuric and nitric acids. The molecular weight of the paraffin previously referred to (p. 99) was found to be 99·3, from which, using the general formula C_nH_{2n+2}, we find the numbers of the carbon atoms by the equation—

$$12n + 2n + 2 = 99{\cdot}3$$
$$n = 6{\cdot}96$$

It was therefore heptane, with the molecular weight 100.

It often happens that by certain processes of oxidation we obtain acids of a known series, such as the fatty acids. If we can get these in a pure state, their molecular weight is easily found by determining the quantity of metal in one of their normal anhydrous salts. The most convenient are the silver salts, as they generally contain no water of crystallisation, and on ignition leave a residue of the pure metal.

If, for example, such a salt contains 51·4 per cent of silver, then, taking the atomic weight of $Ag = 107·7$, its molecular weight is—

$$\frac{100 \times 107·7}{51·4} = 209·4$$

It differs from the acid by containing one atom of metal in the place of one atom of hydrogen, and the acid has, consequently, the molecular weight—

$$(209·4 - 107·7) + 1 = 102·7$$

The general formula of the acids being $C_nH_{2n}O_2$, we find n in this case as follows—

$$12n + 2n + 32 = 102·7$$

$$n = \frac{102·7 - 32}{14} = 5 \text{ (nearly).}$$

The body is, therefore, valerianic acid, $C_5H_{10}O_2$.

If we have to do with an amine of the series $C_nH_{2n+3}N$, we combine its hydrochloride with platinic chloride, and obtain thus a compound corresponding to ammonium platinichloride $(NH_4)_2PtCl_6$, and having the general formula $(C_nH_{2n+4}N)_2PtCl_6$, which, on ignition, leaves a quantity of pure platinum behind, from which we can easily calculate the value of n.

In most cases, however, we do not know that the compound belongs to a definite group, and if it is not volatile without decomposition the only way of ascertaining its molecular formula has been, until recently, a study of its chemical properties and transformations. If an acid, we must find its basicity and analyse several of its salts. We proceed in a similar way with basic compounds, and are thus enabled to ascertain the molecular formula with more or less certainty. Most carbon compounds are neither acids nor bases, and we are obliged to study their chemical metamorphoses and endeavour either to resolve them into more simple molecules or to build them up from these.

To this class belongs cane-sugar, for which, from its percentage composition, we may calculate a number of formulæ, as $C_{11}H_{20}O_{10}$, $C_{12}H_{22}O_{11}$, $C_{13}H_{24}O_{12}$, etc.

If we boil cane-sugar with dilute sulphuric acid, it is resolved into equal parts of grape-sugar or dextrose and fruit-sugar or laevulose, which differ in their physical and chemical properties, but have exactly the same composition—

Carbon . . .	40·0
Hydrogen . . .	6·6
Oxygen . . .	53·4
	100·0

On dividing these numbers by the atomic weights, we get the ratio—

$$C : H : O = 3{\cdot}3 : 6{\cdot}6 : 3{\cdot}3 = 1 : 2 : 1$$

The most simple formula is, therefore, CH_2O. Now this cannot represent the molecule, because a body having so simple a constitution would be readily volatile, and in fact such a compound is known in formaldehyde, which is gaseous at the ordinary temperature. The two sugars are not volatile but are completely decomposed by heat, a fact pointing to a high molecular weight.

If we divide the numbers obtained in the analysis of cane-sugar by the atomic weights we arrive at the ratio:

$$C : H : O = 3{\cdot}5 : 6{\cdot}4 : 3{\cdot}2$$

From this it appears, that on its decomposition into the other sugars, cane-sugar takes up the elements of water, but how much of it comes into play, we cannot ascertain from the analytical data.

Both grape-sugar and fruit-sugar undergo fermentation, being resolved into equal molecules of carbon dioxide, CO_2, and alcohol, C_2H_6O; hence their molecular formula cannot be less than $C_3H_6O_3$. If we now calculate how many atoms of hydrogen and oxygen are contained in cane-sugar for each three atoms of carbon, we arrive at the formula $C_3H_{5\cdot5}O_{2\cdot75}$; and as the number of hydrogen atoms must be even, the most simple formula for cane-sugar is $C_{12}H_{22}O_{11}$. This readily explains the formation of the two other sugars—

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$$

Other facts lead us to the same formula. Liebig showed that by warming a sugar solution with potassium permanganate, we obtain normal potassium oxalate, manganese dioxide and water, which are formed in accordance with the equation—

$$C_{12}H_{22}O_{11} + 12KMnO_4 = 6K_2C_2O_4 + 12MnO_2 + 11H_2O$$

From these facts it appears that the molecular weight of the different sugars cannot be less than that expressed by the above formulæ; that it is not greater seems to be highly probable from the following observations.

Nearly related to the sugars is mannite or mannitol, which was first discovered in manna, and which most probably, like the sugars, contains six or a multiple of six carbon atoms in the molecule. Its analysis leads to the formula $C_6H_{14}O_6$, which must be its molecular formula; it cannot be half, or else it would contain an uneven number of hydrogen atoms; it cannot be double, because no carbon compound can contain more hydrogen atoms than a paraffin with an equal number of carbon atoms, the boundary line being drawn by the formula C_nH_{2n+2} The further investigation of mannitol showed it to be the alcohol of a hexad radical, and to have the constitution $C_6H_8(OH)_6$. It must be regarded as a derivative of hexane, and indeed it is converted into this paraffin by heating it with an excess of hydriodic acid—

$$C_6H_8(OH)_6 + 12HI = C_6H_{14} + 6H_2O + 6I_2$$

It has further been found that by the action of sodium amalgam, an aqueous solution of fruit-sugar is converted into mannitol, whilst grape-sugar, under the same conditions, yields a similar compound which has the same composition as mannitol, and, like the latter, is an alcohol of a hexad radical.

As the last example we will take aurin (see p. 102). It is produced by heating phenol with oxalic acid and sulphuric acid. Now as oxalic acid is resolved by the action of hot sulphuric acid into water, carbon monoxide, and carbon dioxide, we must conclude that one of the two latter compounds acts on the phenol to form aurin, and if we try to explain its formation by a simple equation, we find that this can be done only by the following—

$$3C_6H_6O + CO_2 = C_{19}H_{14}O_3 + 2H_2O$$

The further examination of aurin has proved that this formula expresses its composition and molecular weight. It combines with hydrogen to form colourless leucaurin or trihydroxy-triphenylmethane, $C_{19}H_{13}(OH)_3$, in which we can replace the hydroxyls by hydrogen and obtain triphenylmethane, $C_{19}H_{16}$, a hydrocarbon of known molecular weight, and easily transformable again into leucaurin and aurin.

These methods for ascertaining the molecular weight of a non-volatile organic compound only give satisfactory results when we already have some idea of its constitution. Otherwise, they will leave us in doubt, and for a long time it has been a desideratum to have as simple a method for ascertaining the molecular weight of non-volatile compounds as we have had in the case of volatile bodies.

The progress of molecular physics has shown that molecules, when contained in a dilute solution, behave similarly to those in the gaseous state. Whilst, according to Avogadro's law, in different gases, under the same conditions of temperature and pressure, the number of molecules is proportional to the volume, it has been shown that *solutions of different bodies in the same solvent, containing in a given volume an equal number of dissolved molecules, show equal osmotic pressures, equal vapour tensions, and the same freezing point.*

This important discovery has given us the means of finding the molecular weight of bodies which do not volatilise without decomposition; and the effect which a body has on the freezing point of one of its solvents has found a practical application, which will certainly yield most important results.

Blagden, as early as 1788, established the fact, with regard to inorganic salts, that the lowering of the freezing point of their aqueous solutions is proportional to the weight of the substance dissolved in a constant weight of water. This law was quite forgotten when, in 1861, it was rediscovered by Rüdorff. In 1871 Coppet again called attention to it, and clearly pointed out that when this lowering of the freezing point is worked out for a determinate quantity of the substance dissolved in 100 grams of water, the result, which he calls the *coefficient of depression*, is constant for the same substance, and the coefficients for different substances bear a simple relation to their molecular weights.

It was left for Raoult to show clearly what these relations are, and to extend the investigation to organic substances, and to other solvents besides water. By his investigations it appears that the lowering of the freezing point is proportional to the weight of substance dissolved in a constant weight of the solvent; in other words the lowering of the freezing point is dependent solely on the respective masses of the substance and solvent, and is independent of the temperature. If the observed depression of the freezing point be taken as C, and the weight of substance dissolved in 100 grammes of the solvent be P, then the quotient $\frac{C}{P} = A$, which Raoult calls the "gross coefficient of depression" (*coefficient d'abaissement brut*), is the lowering of the freezing point produced by 1 gramme of substance dissolved in 100 grammes of water. By multiplying A by the molecular weight of the substance we obtain the depression which would be produced by 1 gramme-molecule of substance dissolved in 100 grammes of the solvent, or the "true molecular depression" (*abaissement moléculaire vrai*), which we call T. We have, therefore

$$T = \frac{C}{P} \times M$$

T is a quantity varying with the solvent, but, with the same solvent, constant for a large group of compounds. It may, therefore, be taken as a known quantity, its value for the following solvents, which are generally used in the determination of molecular weights, being

	T
Water . .	19
Acetic acid .	39
Benzene . .	49

We have, therefore, only to find the A or the coefficient of depression of the freezing point, in order to calculate the molecular weight by the formula

$$M = \frac{T}{A}$$

We will take an example—

6·064 grms. of cane-sugar were dissolved in 96·28 grms. of water, and the freezing point of the solution was found to be −0·355° C., we find A—

$$\frac{0·355 \times 96·28}{6·064 \times 100} = 0·056.$$

Therefore the molecular weight is

$$\frac{19}{0{\cdot}056}=340$$

From the formula $C_{12}H_{22}O_{11}$, we calculate 342.

By the same method the molecular weights of other sugars were determined—

	Calc.	Found.
Mannitol, $C_6H_{14}O_6$ . .	182	181
Grape-Sugar, $C_6H_{12}O_6$ . .	180	180·2

Brown and Morris have also shown that in this way we may demonstrate the splitting up of the molecule of cane sugar by the action of dilute acids, the gross coefficient of depression of the solution being 0·058, and corresponding to the molecular weight 328, after treatment with an acid becomes 0·109, from which we calculate the molecular weight 175.[1]

Of still greater importance is it that Raoult's method will enable us to find the molecular weight of such highly complicated substances as starch and albumen. In this case many difficulties have yet to be overcome. Some experiments of Brown and Morris have shown that the molecular weight of starch is higher than 20,000, while, for other reasons, they assume its molecular formula to be $C_{1200}H_{2000}O_{1000}$, corresponding to a molecular weight of 32,400.[2]

After having found the *empirical* molecular formula of a compound, our next endeavour is to ascertain its *rational* formula. This term was introduced by

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[1] *Journ. Chem. Soc.* 1888, 1, 610.

[2] *Ibid.* 1889, 1, 462.

Berzelius, who understood by it a formula which should represent the *constitution* of the compound—in other words, a formula expressing its relations to other bodies, or pointing out its past and its future. For the theoretical chemist the substance itself has only a subordinate interest; he wishes to know in what relation it stands to its progenitors and its progeny.

"It is obvious that we cannot neglect a description of the body; we must know its physical properties, for they serve us as characteristics by which we recognise it and as a criterion of its purity; they are its proofs of identity."[1]

Strictly speaking, these descriptive details do not belong to the province of pure chemistry, and at no distant time they will form a branch of descriptive mineralogy.

We have already seen that with the progress of chemistry the rational formulæ continually changed, and that it was assumed one compound could have more than one rational formula. Kekulé, writing in 1859, said, "Which of the different rational formulæ we shall make use of in a definite case is essentially a matter of convenience. From what has been stated, the right of assuming different rational formulæ cannot be doubted. At the same time we must not forget that *rational formulæ* are nothing more than formulæ expressing certain reactions. They do not express the constitution of the body; they are only expressions for the metamorphoses of a body and a comparison of different bodies, and are in no wise intended as an expression of the constitution or the arrangement of the atoms in the actual substance."[2]

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[1] Kekulé, *Lehrbuch*, 1, 4.

[2] *Ibid.* 1, 157.

And yet at the same time he propounded the two principles which form the foundation of our present theory; viz. *that carbon is a tetrad element and that its atoms have the property of combining with each other.*[1]

Somewhat later, similar views were published by Couper, apparently in ignorance of Kekulé's paper. He says, speaking of carbon:—

"This body is found to have two highly distinctive properties:

"1. It combines with equal numbers of equivalents of hydrogen, chlorine, oxygen, sulphur, etc.

"2. It enters into chemical union with itself.

"These two properties, in my opinion, explain all that is characteristic of organic chemistry. This will be rendered apparent as I proceed.

"The second property is, so far as I am aware, here signalised for the first time. Evidence as to its being a property of carbon may therefore be required.

"It will be found in the following: What is the link which binds together bodies composed of 4, 6, 8, 10, 12, etc. equivalents of carbon, and as many equivalents of hydrogen, oxygen, etc.? In these you may, perhaps, remove all the hydrogen or oxygen, and substitute so many equivalents of chlorine, etc. It is then the carbon that is united to carbon."

He then shows that neither hydrogen nor oxygen can be the binding element, and continues: "All the countless instances of substitution by chlorine, etc., tend in the same direction. They prove beyond doubt that carbon enters into chemical union with carbon, and that in the most stable manner.[2]

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[1] Kekulé, *Lehrbuch*, 1, 161; *Ann. Chem. Pharm.* 106, 151.

[2] *Phil. Mag.* (4) 16, 104; Couper still used the old atomic weights of carbon, oxygen, etc.

Such considerations led to the *law of the linking of atoms.*

Whilst formerly it was supposed that the different atoms forming a molecule were kept together by each atom attracting all the others or a certain number of them, and these again exercising a reciprocal attraction on the first atom, and keeping it in its place, the conviction now arose that this attraction goes only from atom to atom. The atoms are, figuratively speaking, linked together in a chain; if one link be removed without being replaced by another, the chain is broken, — the compound undergoes decomposition.

The links of such a chain do not consist of equivalent atoms; a monad has only one hasp, a dyad two, etc.

The constitution of the carbon compounds now admits of a simple explanation.

Kekulé pointed out, that if two carbon atoms combine, the most simple, and therefore the most probable case is, "that *one* combining unit of *one* carbon atom enters into combination with *one* combining unit of the *other.* Of the $2 \times 4 = 8$ combining units of the two carbon atoms, *two* are employed in keeping these two atoms together; and six combining units remain, which may be tied by the combining units of other atoms. In other words, a group of two carbon atoms fastened together in this way will be hexabasic or hexatomic; it will form a compound with six atoms of a monatomic element, or in general with so many atoms, that the sum of their valency units is $= 6$."

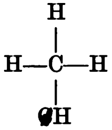
"If more than two carbon atoms combine, the new ones may attach themselves in the same manner, so that one-fourth of the affinity of one atom is bound by one-fourth of the affinity of another atom. For each new carbon atom entering the group its basicity is increased by two."

"The number of hydrogen atoms combined with n carbon atoms will, therefore, be expressed by the formula—

$$2 + n(4 - 2) = 2 + 2n."$$

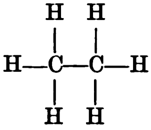
We thus obtain the homologous series of the paraffins; their constitution can be expressed graphically as follows—

Methane.



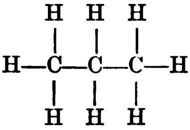
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

Ethane.



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Propane.



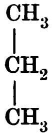
$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

etc.

or, more simply—

CH_4

$$\begin{array}{c} CH_3 \\ | \\ CH_3 \end{array}$$



$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_3 \end{array}$$

By replacing in a paraffin one atom of hydrogen by an element or a monad group of atoms, we obtain the compounds of the monad alcohol radicals C_nH_{2n+1}. Couper used similar graphic formulæ; those employed by Kekulé in his *Lehrbuch* are different.

Other chemists, again, who developed the law of the linking of atoms, wrote formulæ expressing the *structure* of compounds in other different ways, and afterwards made claims of priority, but without much justification. Lothar Meyer has pointedly remarked: "By the establishment of these two principles (p. 114) the arrangement of the formulæ of all possible carbon compounds was also established. The mode of writing these formulæ was reduced to a problem of the calculus of combination, permutation, and variation solved long ago, and its application to concrete cases did not require an extraordinary acuteness or a great inventive talent. It is quite a matter of taste or convenience, and of a very subordinate importance, whether we write the series of symbols by which we express the arrangement of the atoms, as ascertained by the above principles, according to the use in Europe from the left to the right, or from the right to the left like the Hebrews, or from the top to the bottom in accordance with the Chinese custom."[1]

For lecture illustrations we often use models; the best known are those devised by Kekulé, consisting of wooden balls of different colours to represent the atoms, whilst the number of connecting rods corresponds to the valency of the different atoms. By linking them together in the proper way, we obtain *glyptic* formulæ.

Eminent chemists have objected to the use of such illustrations on the ground that they might lead the pupils to believe that the atoms had such a shape, or to imagine they were connected by material bonds. Dalton used square wooden blocks of different colours for illustrating his atomic theory, and it happened indeed, that a dunce, when asked to explain the atomic theory, said: "Atoms are square blocks of wood invented by Dr. Dalton."

But we might as well object to the use of diagrams

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[1] *Ann. Chem. Pharm.* 145, 124.

or models for illustration of the parallelogram of forces, or, as Henry Watts has said: "to that of an artificial globe in teaching geography, lest the student should acquire curious notions about the *brazen* meridian, or the *wooden* horizon."[1]

Graphic and glyptic formulæ are of course hardly needed for explaining the constitution of the more simple carbon compounds. But they are of value in the case of more complicated ones, and principally for illustrating the different constitution of numerous compounds having the same percentage composition, but very different properties.

[1] Fownes's *Chem.* 12 Ed. i. 258.

VII

Methods for determining the constitution of organic compounds—History of lactic acid—Isomerism.

We will now explain, by some simple examples, the means we have for ascertaining the constitution of a compound.

Ethyl alcohol, C_2H_6O, is a derivative of ethane, and, as Frankland has shown, can be easily converted into this hydrocarbon. By heating with hydriodic acid, alcohol yields ethyl iodide—

$$C_2H_6O + HI = C_2H_5I + H_2O$$

This, when heated with zinc and water under pressure, changes into ethane—

$$C_2H_5I + H_2O + Zn = C_2H_6 + Zn(OH)I$$

If we act on ethane with chlorine, we obtain ethyl chloride—

$$C_2H_6 + Cl_2 = C_2H_5Cl + HCl$$

On heating the latter with potash we get again ethyl alcohol—

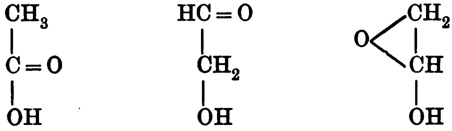
$$C_2H_5Cl + KOH = C_2H_5.OH + KCl$$

Ethyl alcohol must, therefore, be considered as ethane, in which one atom of hydrogen is replaced by the monad radical hydroxyl, OH.

By the oxidation of alcohol we obtain acetic acid, two atoms of hydrogen being replaced by hydrogen. The question now arises which two of the six hydrogen atoms are thus substituted by oxygen; but the inquiry is limited by the fact that acetic acid, like alcohol, contains one hydroxyl. This can be proved by several reactions. Thus, by the action of phosphorus pentachloride on most hydroxyl compounds, this radical is exchanged for chlorine, alcohol being converted into ethyl chloride, and acetic acid into acetyl chloride, C_2H_3OCl, which, by the action of water, is again resolved into hydrochloric acid and acetic acid—

$$C_2H_3OCl + H_2O = C_2H_3O.OH + HCl$$

The latter, therefore, is derived from alcohol by hydrogen of the ethyl, being replaced by oxygen, and consequently the constitution of acetic acid will be expressed by one of the following formulæ—



$$\begin{array}{l} CH_3 \\ | \\ C=O \\ | \\ OH \end{array} \qquad \begin{array}{l} HC=O \\ | \\ CH_2 \\ | \\ OH \end{array}$$

To decide between these, we make use of two general methods; we either try to resolve the molecule into smaller groups of known constitution or to build it up from such.

If we heat acetic acid with an excess of an alkali, it is decomposed with the formation of a carbonate, and marsh gas—

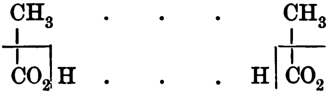
$$C_2H_3NaO_2 + NaOH = Na_2CO_3 + CH_4$$

By passing an electric current through a concentrated solution of potassium acetate, we obtain free hydrogen, potassium hydrogen carbonate, and ethane—

$$2C_2H_3KO_2 = 2KHCO_3 + H_2 + C_2H_6$$

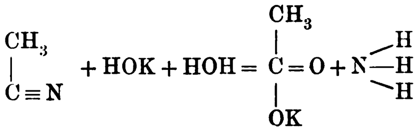
This decomposition is readily explained. When a salt is decomposed by electrolysis it is first resolved simply into the metal, and the residue of the molecule. In the case of potassium acetate, the metal, which is set free, acts on the water with the liberation of hydrogen and formation of caustic potash, while the group $C_2H_3O_2$ splits up into carbon dioxide and methyl, CH_3. The latter, however, cannot exist in the free state and combines with another methyl to form ethane, whilst the former saturates the caustic potash.

These decompositions make it highly probable that one of the two linked carbon atoms of acetic acid is combined with hydrogen only, and consequently the constitution is expressed by the first formula, by which the formation of marsh gas and ethane is simply explained



$$\begin{array}{lcr} CH_3 & \ldots & CH_3 \\ | & & | \\ CO_2 \mid H & \ldots & H \mid CO_2 \end{array}$$

As further proof we have the synthesis of acetic acid from methyl compounds. By the action of hydriodic acid on methyl alcohol we obtain methyl iodide, which, on heating with potassium cyanide is converted into methyl cyanide or acetonitrile. On boiling this with potash solution it changes into potassium acetate—

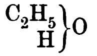


$$\begin{matrix}CH_3\\ |\\ C\equiv N\end{matrix} + HOK + HOH = \begin{matrix}CH_3\\ |\\ C=O\\ |\\ OK\end{matrix} + N\begin{matrix}\diagup H\\ -H\\ \diagdown H\end{matrix}$$

The contracted formula of acetic acid, $CH_3 . CO . OH$ is identical with that of Berzelius, and of the theory of types. According to Berzelius, acetic acid is oxalic acid coupled with methyl, while the theory of types assumed that carbonyl combined with methyl to form $CO . CH_3$, and this group replaced one atom of hydrogen in one molecule of water. To-day we explain its constitution by supposing that it contains two carbon atoms linked together by one combining unit of each, the three remaining units of one atom being saturated by hydrogen, and those of the second with two atoms of oxygen in such a way, that one oxygen atom is linked to the carbon by both of its combining units and the second only by one, whilst the other unit is combined with hydrogen.

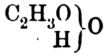
Another instructive example is afforded by lactic acid, because it clearly shows how the theory of types gradually changed into that of the linking of the atoms. Lactic acid was discovered in 1780 by Scheele in sour milk, and further examined by Berzelius, and chiefly by Liebig, and by Mitscherlich, who, having established its composition, and examined its salts, arrived at the formula $C_3H_6O_3$. This was afterwards confirmed by its synthesis, which Strecker discovered, and which will be discussed later. For theoretical reasons, however, this formula was doubled by Gerhardt, a change to which most chemists agreed until Wurtz found that lactic acid was also formed by the oxidation of propyl glycol or the alcohol of dyad propylene, C_3H_6. Its formation appeared, therefore, quite analogous to that of acetic acid from ethyl alcohol, and Wurtz expressed the relations of these compounds to each other by the following typical formulæ :—

Ethyl alcohol.



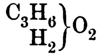
$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$$

Acetic acid.



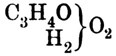
$$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$$

Propylene glycol.



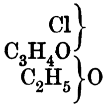
$$\left.\begin{matrix}C_3H_6\\H_2\end{matrix}\right\}O_2$$

Lactic acid.



$$\left.\begin{matrix}C_3H_4O\\H_2\end{matrix}\right\}O_2$$

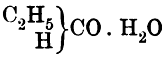
Acetic acid being monobasic, Wurtz concluded that lactic acid was dibasic, and this view appeared to be confirmed by the fact that phosphorus chloride converted the acid into lactyl chloride, $C_3H_4OCl_2$. On treating this with ethyl alcohol, the ethyl ether of chlorolactic acid was obtained, having the following rational formula :—[1]



$$\begin{array}{l}Cl\rbrace\\ C_3H_4O\\ C_2H_5\rbrace O\end{array}$$

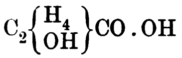
Kolbe opposed these views. According to him the glycols were not alcohols, inasmuch they did not yield aldehydes on oxidation. They were oxyhydrates, and lactic acid an oxyacid :—

Propylene oxide hydrate.



$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}CO\,.\,H_2O$$

Oxypropionic acid.



$$C_2\left\{\begin{matrix}H_4\\OH\end{matrix}\right\}CO\,.\,OH$$

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[1] *Ann. Chem. Pharm.* 107, 194.

In other words, lactic acid was propionic acid with one atom of hydrogen replaced by hydrogen peroxide.[1] The assumption that the latter could play the part of a simple body and replace hydrogen might appear in the first moment so paradoxical and improbable as to arouse a vigorous opposition. Yet in recent chemistry similar cases had been observed, such as the substitution of chlorine or hyponitric acid for hydrogen, which appeared no less paradoxical, and yet had found general acceptance.

Lactyl chloride was regarded by Kolbe as chloropropionyl chloride, and the compound obtained from it by the action of ethyl alcohol was the ether of chloropropionic acid. This was proved experimentally at the time by Ulrich in Kolbe's laboratory. Wurtz had stated that lactyl chloride might be converted again into lactic acid by acting on it with water. Ulrich found that this reaction only took place in the presence of a strong base, while water alone resolved it into hydrochloric acid and chloropropionic acid. By treating the latter with nascent hydrogen he converted it into propionic acid, which is monobasic, as are also chloropropionic and oxypropionic acid.[2]

Wurtz replied, saying that the substitution of the group HO for chlorine, and therefore for hydrogen, had been known for a long time. This group was simply a water-residue; to regard it as hydrogen peroxide was quite an unwarrantable hypothesis.[3]

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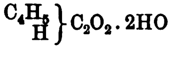
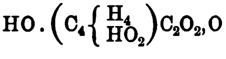
[1] Kolbe used the old atomic weights and wrote these formulæ as follows:—

Propylene glycol.



$$\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}C_2O_2.2HO$$

Lactic acid.



$$HO.\left(C_4\left\{\begin{matrix}H_4\\HO_2\end{matrix}\right.\right)C_2O_2,O$$

[2] *Ann. Chem. Pharm.* 109, 257.

[3] *Répert Chim.* 1, 343.

The argument that the aldehydes of the glycols were unknown was of no significance, for that of methyl alcohol was also not known.

But lactates containing two equivalents of a metal existed, such as tin lactate, which had been prepared by Brüning.[1]

As a new and convincing proof of the dibasic nature of lactic acid, Wurtz mentioned that he had succeeded in obtaining the diethyl-ether of lactic acid, the formation of such a compound being, as Gerhardt had shown, highly characteristic of a dibasic acid.

Wurtz now made a distinction between basicity and atomicity. The following compounds were diatomic:—

Glycol.	Glycollic acid.	Oxalic acid.
$\left.\begin{matrix}C_2H_4\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}C_4H_2O\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}C_2O_2\\H_2\end{matrix}\right\}O_2$

Glycol was a neutral body, glycollic acid a strong monobasic, and oxalic acid a strong dibasic acid, the basicity increasing with an increase of oxygen. Glyceric acid, which Debus had obtained by the oxidation of glycerin, was, according to Wurtz, a monobasic triatomic acid—

Glycerin.	Glyceric acid.
$\left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\}O_3$	$\left.\begin{matrix}C_3H_3O\\H_3\end{matrix}\right\}O_3$

The formation of lactic acid from propylene glycol corresponded to that of glycollic acid from common

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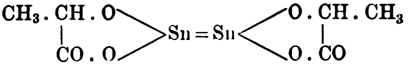
[1] This salt has probably the following constitution:—

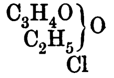


glycol, both behaving as strong monobasic acids. For the reasons given above, Wurtz assumed that lactic acid could also perform the function of a weak dibasic acid.[1]

Strecker, as already mentioned, discovered a synthesis of lactic acid. By heating aldehyde-ammonia, $C_2H_4O . NH_3$, with prussic acid and hydrochloric acid, he obtained a compound which he called alanin, $C_3H_7NO_3$, which, by the action of nitrous acid, is converted into lactic acid. Kolbe recognised alanin as amidopropionic acid, and obtained it by heating chloropropionic ether with ammonia ; his pupil Lautemann succeeded in reducing lactic acid to propionic acid by heating it with hydriodic acid.

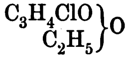
According to Kolbe, all these compounds were nearly related to each other; they had a similar constitution or belonged to the same chemical type, since by the most simple processes of substitution, they might be changed one into another, forwards or backwards. Wurtz was of opinion that the name chlorolactic ether was as appropriate as chloropropionic ether; by the first was expressed the fact that chlorine might be replaced by compound radicals, and by the second that this compound formed the connecting link between the lactic and propionic series. We might, therefore, give two rational formulæ to it, according to the reactions which we wished to express—

Chlorolactic ether.



$$\begin{matrix}\left.\begin{matrix}C_3H_4O\\C_2H_5\end{matrix}\right\}O\\Cl\end{matrix}$$

Chloropropionic ether.



$$\left.\begin{matrix}C_3H_4ClO\\C_2H_5\end{matrix}\right\}O$$

"I confess," says Kolbe, "that I do not possess

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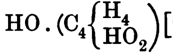
[1] *Bull. Soc. Chim.*, 13th March 1859.

such an elastic chemical conscience, and I would never subscribe to such a dogma, even if something more than a weak hypothesis were at stake. I am of opinion that Wurtz, by these words, has pronounced the doom of his theory."

Kolbe now regarded propionic acid and lactic acid as derivatives of carbonic acid—[1]

$[C_2O_2]O_2$, Carbonic acid.
$HO\,.\,(C_4H_5)[C_2O_2],\ O$, Ethyl-carbonic or propionic acid.

$HO\,.\,\left(C_4\left\{\begin{matrix}H_4\\HO_2\end{matrix}\right.\right)[C_2O_2],\ O$, Oxyethyl-carbonic or lactic acid.

He maintained that dibasic acids form neutral and acid salts or ethers, monobasic amido-acids, and diamides; that lactic acid does not; that for ascertaining the saturating capacity of an acid, the salts of tin or other heavy metals were quite inappropriate; that Wurtz's ethyl lactate was the ethyl-ether of oxyethyl propionic acid, etc.[2]

Wurtz said in his reply that from his experiments it could not be doubted that lactic acid was a dibasic acid, if only a weak one, and he brought forward, as a new argument, the fact that on heating it yielded an anhydride, while no monobasic acid was known, which by the action of heat was resolved into water and an anhydride.[3]

Kolbe's view was correct; lactic acid is hydroxypropionic acid, but he missed its relation to propylglycol; the idea did not strike him that the glycols are alcohols of dyad radicals.

While this controversy was still going on Kekulé published the first part of his handbook, in which he showed how easily the constitution of lactic acid could

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[1] $C=6$; $O=8$.

[2] *Ann. Chem. Pharm.* 113, 223.

[3] *Ann. Chim. Phys.* (3), 59, 161.

be explained by going back from the radicals to the atoms. He still used typical formulæ, but nothing is easier than to transcribe them into graphic formulæ.[1]

Lactic acid contains two typical or extra-radical hydrogen atoms, which differ from each other just as the typical hydrogen atom of acetic acid differs from that of alcohol. One of them is, therefore, easily replaced by metals, just as the extra-radical hydrogen atom of the monobasic acid, while the second may be exchanged for acid radicals, like that of the alcohols. Lactic acid is, at the same time, a monobasic acid and an alcohol; it is propionic acid, in which one hydrogen atom of the ethyl is replaced by hydroxyl, and its formula is, therefore, $C_2H_4(OH)CO.OH$. By phosphorus chloride it is converted into chloropropionyl chloride, $C_2H_4Cl.COCl$, which, like other acid chlorides, is resolved by water into hydrochloric acid and chloropropionic acid, $C_2H_4Cl.CO.OH$. On heating ethyl chloride with potash we get ethyl alcohol; by the same reaction chloropropionic acid is converted into hydroxypropionic acid or lactic acid, and, just as ethylamine is formed when ethyl chloride is heated with ammonia, so the latter converts chloropropionic acid into amidopropionic acid, $C_2H_4(NH_2)CO.OH$.

When an alcohol is heated with an acid it yields an ethereal salt or ester; from ethyl alcohol and acetic acid we obtain ethyl acetate or acetic ester—

$$CH_3.CO.OH + HO.C_2H_5 = CH_3.CO.O.C_2H_5 + H_2O$$

A similar reaction takes place when lactic acid is heated alone, for it is at the time an acid and an alcohol, and we obtain an ethereal salt, which has been called lactic anhydride or lactide—

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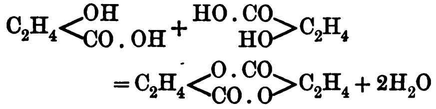
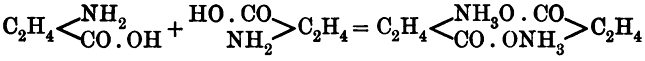
[1] Ladenburg, *Entwicklungsgeschichte der Chemie*, 2nd ed. 278.



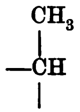
$$C_2H_4\left<\begin{matrix}OH\\CO.OH\end{matrix}\right. + \left.\begin{matrix}HO.CO\\HO\end{matrix}\right>C_2H_4$$
$$= C_2H_4\left<\begin{matrix}O.CO\\CO.O\end{matrix}\right>C_2H_4 + 2H_2O$$

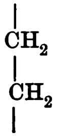
Whilst lactic acid is an alcohol and an acid, amidopropionic acid is, at the same time, an amine and an acid; it combines, therefore, with acids, and at the same time the hydrogen of the acid hydroxyl can be replaced by metals. In the free state, however, it is perfectly neutral, because the acid part combines with the basic part, forming a salt having the following constitution:—



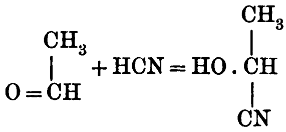
$$C_2H_4\left<\begin{matrix}NH_2\\CO.OH\end{matrix}\right. + \left.\begin{matrix}HO.CO\\NH_2\end{matrix}\right>C_2H_4 = C_2H_4\left<\begin{matrix}NH_3O.CO\\CO.ONH_3\end{matrix}\right>C_2H_4$$

In order to get a graphic formula for lactic acid we must know the constitution of the group C_2H_4. This will be represented by one of the following formulæ:—



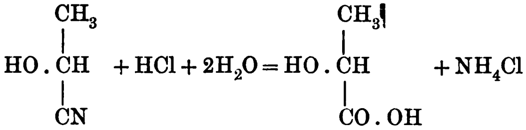


We can easily decide between these two; lactic acid, on oxidation, is resolved into carbon dioxide and acetic acid; the latter contains methyl, and as this group cannot be formed by oxidation, it must, therefore, be present in lactic acid. We are led to the same conclusion by Strecker's synthesis, which, in a simplified form, is effected by heating a mixture of aldehyde and hydrocyanic acid with hydrochloric acid. Aldehyde is the first product of oxidation of ethyl alcohol; it combines with oxygen to form acetic acid, and with hydrogen to form alcohol again, its constitution being thus established. It unites with hydrocyanic acid to form hydroxypropionitrile—



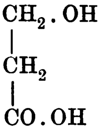
$$\begin{array}{l}CH_3\\ |\\ O=CH\end{array} + HCN = \begin{array}{r}CH_3\\ |\\ HO.CH\\ |\\ CN\end{array}$$

By heating this with hydrochloric acid, we obtain lactic acid—



$$\begin{array}{r}CH_3\\ |\\ HO.CH\\ |\\ CN\end{array} + HCl + 2H_2O = \begin{array}{l}\quad\;\; CH_3\\ \quad\;\; |\\ HO.CH\\ \quad\;\; |\\ \quad\;\; CO.OH\end{array} + NH_4Cl$$

According to our theory there can exist an acid having the same composition as lactic acid and the following constitution:—



$$\begin{array}{l}CH_2.OH\\ |\\ CH_2\\ |\\ CO.OH\end{array}$$

This compound is known, and, as already stated, we find among the carbon compounds a large number of bodies having the same percentage composition and very different physical or chemical properties.

The first example was observed in 1820 by Dalton, who found in the gas, which is obtained by the distillation of fatty oils, a hydrocarbon which combines with chlorine like olefiant gas. He suspected that its "atom" contained twice as much carbon and hydrogen as the latter gas, and when, in the following year, his friend W. Henry found such a hydrocarbon in coal gas, Dalton said that the hydrocarbon from oil-gas which for the present he would call superolefiant gas was a gas *sui generis* consisting of the elements of olefiant gas, but differing in the number of atoms. "Most probably the atom of the new gas consists of two of olefiant gas."[1]

This supposition was soon confirmed by Faraday. Oil-gas, which had been introduced for illuminating purposes by Taylor in 1815, was pumped under a pressure of thirty atmospheres into vessels, which were sent to the houses of the consumers by the Portable Gas Company. By this pressure a portion of the gas condensed into a liquid, which Faraday found to be a mixture of hydrocarbons. One of these, which remained liquid under atmospheric pressure, he called bi-carburet of hydrogen, and this is now known as benzene. The second was a new carburet of hydrogen; he isolated it by gently heating the original liquid, and passing the vapour through a tube at 0° F., when it condensed to a liquid, which began to boil upon a slight elevation of temperature and was all resolved into vapour or gas, before it had attained 32° F. He determined its composition and specific gravity, and found that it contained carbon and hydrogen in the same proportion as olefiant gas, but had twice its density. Thus Dalton's supposition was confirmed. Faraday further showed that, like olefiant gas, it combines with an equal volume of chlorine, and says: "In reference to the existence of

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[1] *Mem. Manch. Lit. Phil. Soc.* (2) 4, 64.

bodies composed of the same elements and in the same proportion, but differing in their qualities, it may be observed, that now we are taught to look for them, they will probably multiply on us."[1] He then refers to the elaborate and beautiful researches of Liebig and Gay-Lussac on the nature of the fulminating compounds of silver, mercury, etc. which led to the conclusion that they were salts of a new acid, consisting of one proportion of oxygen, one of nitrogen, and two of carbon; or of one of oxygen, and one of cyanogen, and therefore to be considered as a true cyanic acid.[2] But Wöhler had obtained from ferro-prussiate of potash a salt which, according to his analysis, is a true cyanate of potash. From this compound other cyanates can be prepared, which have nothing in common with the fulminates but their composition,[3] and Gay-Lussac had pointed out in a footnote, that if Wöhler's analysis were correct, the difference could only be accounted for by ascribing a different mode of combination.

Berzelius, in discussing these interesting results in his annual report, said that an exact knowledge of this point, *i.e.* that bodies exist having the same composition, but very different properties, was of such importance and would have such an influence on organic chemistry, that it could not be accepted as settled before it had undergone the most strict investigation. Carbon and hydrogen combined in such manifold proportions that it was possible a mixture of two nearly equally volatile substances might be taken for a pure compound, and hydrocarbons were, therefore, not suited to decide this question. This would only

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[1] *Phil. Trans.* 1825, 440.

[2] *Ann. Chim. Phys.* (2) 24, 294; 25, 285.

[3] *Ibid.* 27, 190.

be done when the relations observed by Faraday were also to be found in the case of other compounds.[1]

Berzelius's character was quite different from that of Dalton, who did not hesitate to found the boldest speculations on the results of a few and not always very accurate experiments. Berzelius, whose accuracy of work has hardly been surpassed, soon renounced the old axiom that bodies having the same composition, in regard to their constituents and the relative quantities of the latter, must have the same chemical properties, for he found that racemic acid had the same composition as tartaric acid, both consisting of the same elements present in the same atomic proportions, and both acids having the same saturating power.

He now wrote: "Experiments of Faraday seemed to show that an exception to this axiom might occur, if two bodies having the same composition differ from each other by one of them containing twice as many simple atoms as the other, although the relative proportion between their elements remains the same. An example of this is seen in the two hydrocarbons, olefiant gas, CH_2, and the other described by Faraday, which is more condensible, and has the composition C_2H_4 and, therefore, a specific gravity twice as great as the former. In this case the identity of composition is only apparent, for the compound atoms are distinctly different, the relative number of the elementary atoms being equal, but the absolute number unequal. More recent experiments have now shown that the absolute, as well as the relative, number, can be equal; yet their combination may take place in such an unlike manner that the properties of bodies having absolutely like composition become unlike.

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[1] *Jahresb.* 6, 102.

To such a result we have been led only very gradually. Thus I showed, some years ago, that two oxides of tin exist, having the same composition but different properties. Soon after it was discovered that Liebig's fulminic acid and Wöhler's cyanic acid had the same composition and the same saturating capacity." Then he gives some other examples, among these tartaric acid and racemic acid—afterwards he also mentions cyanate of ammonia and urea—and continues: "Mitscherlich's remarkable discovery, that bodies composed of different elements, but containing the same number of them and having them arranged in the same manner, crystallise in the same form, or are isomorphous, as we now say, has thus received its complement; and this complement consists in the discovery that bodies exist composed of an equal number of atoms of the same elements arranged, however, in an unlike manner and possessing therefore different chemical properties and crystalline forms, that is, they are heteromorphous." Such bodies he proposed to call *isomeric* (ἰσομερής, composed of equal parts).[1]

Olefiant gas and Faraday's hydrocarbon do not belong to this class, because, although the relative number of their atoms is the same, the absolute number is not, they have a different atomic weight and may, therefore, be called *polymeric* (πολύς, several).

But there exists a third class of bodies, which apparently are isomeric, but differ from the true isomeric compounds in being made up of two unlike parts, such as stannous sulphate, SnO, SO_3, and basic stannic sulphite, SnO_2, SO_2 if the latter existed (which he did not know); or cyanic acid, a combination of water with an oxide of cyanogen, and cyanuric acid,

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[1] *Jahresb.* 11, 44; *Pogg. Ann.* 19, 326.

which Berzelius regarded as an oxide of the ternary radical CNH. These two compounds change easily one into the other, and so do other bodies, made up of two different compounds. Berzelius, therefore, calls them *metameric* (μετά in the same sense as in metamorphosis).[1]

Since that time we have become acquainted with a large number of such bodies. Many of these, such as the isomeric alcohols and fatty acids, were foreseen by Kolbe's prophetic eye; but his theory led him sometimes to predictions which were not in accordance with the law of the linking of atoms, and were not fulfilled. To-day this law enables us to explain most cases of isomerism; certain apparent exceptions have disappeared with the progress of science, and others will doubtless share their fate.

We must not forget that our present theory is not a dogma, but is changing continually according to the law of dialectic.

The progress which has been made during the last thirty years is best seen by comparing our present views with those formerly held. Kekulé says:[2]

"We denote by the general term *isomeric* such bodies as have the same percentage composition and different properties.

"We call those substances *polymeric* in which the isomerism is conditioned by differing molecular weights; they have the same empirical formula, but not the same molecular formulæ."

To these belong, among others, the olefines.

"We use the term *metameric* for those isomeric bodies having the same molecular weight, of which we can give some account by the difference in the

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[1] *Jahresb.* 12, 63.

[2] *Lehrb.* 1, 183.

relative position of the atoms; or they are bodies having the same empirical molecular formulæ, but different rational formulæ."

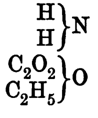
The number of these is very large; he includes among them—

The alcohols and their ethers.
The fatty acids and their esters.
The amines.
The compound ureas.
The homologues of oxalic acid and their esters, etc.

Thus propyl alcohol is metameric with methyl-ethyl ether; propionic acid with methyl acetate and ethyl formate; propylamine with methyl-ethylamine and trimethylamine, etc.

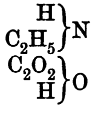
"In all these and numerous other cases we explain the metamerism by the difference of the radicals contained in the compounds. In some other cases we find that metameric bodies contain the same radicals, but we can give an explanation of the cause of their isomerism; the same radicals are grouped differently in the molecule—

Oxamethane.



$$\left.\begin{matrix}H\\H\end{matrix}\right\}N \quad \left.\begin{matrix}C_2O_2\\C_2H_5\end{matrix}\right\}O$$

Ethyloxamic acid.



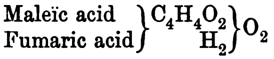
$$\left.\begin{matrix}H\\C_2H_5\end{matrix}\right\}N \quad \left.\begin{matrix}C_2O_2\\H\end{matrix}\right\}O$$

"Whilst in all these cases we can form a certain conception of the cause of isomerism by means of rational formulæ which are founded on the behaviour of the respective bodies, or explain them by polymerism or metamerism, there exists a comparatively large number of isomers of which in the present state of our knowledge we can find no explanation, or at least only a partial explanation.

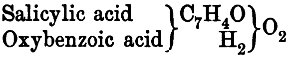
"The reason is that in many cases, one or both of the isomeric bodies have not been sufficiently studied for us to be able to express their chemical behaviour by rational formulæ. On the other hand we find that different bodies, to which we must assign, according to the present state of our knowledge, the same rational formula, possess different properties. Such cases have sometimes been called *isomeric in the restricted sense* of the word (*isomer im engeren Sinne*)."

Among these Kekulé places the carbohydrates, such as starch, dextrin, gum, and cellulose, all having the empirical formula $C_6H_{10}O_5$, and the sugars, $C_{12}H_{22}O_{11}$, to which belong cane-sugar and milk-sugar.

To these he adds the large number of essential oils of the formula $C_{10}H_{16}$, and different compounds having the same typical formula, as, for example—



$$\left.\begin{array}{l}\text{Maleïc acid}\\ \text{Fumaric acid}\end{array}\right\}\left.\begin{array}{c}C_4H_4O_2\\ H_2\end{array}\right\}O_2$$



$$\left.\begin{array}{l}\text{Salicylic acid}\\ \text{Oxybenzoic acid}\end{array}\right\}\left.\begin{array}{c}C_7H_4O\\ H_2\end{array}\right\}O_2$$

"To the most remarkable examples of unexplained isomerism belong those comparatively simple chlorides of which one is produced by the action of phosphorus superchloride on aldehyde, and the other by the direct union of ethylene with chlorine, or by the action of phosphorus superchloride on glycol. Both by their mode of formation and their behaviour they must be regarded as chlorides of diatomic radicals having the same rational formula—

Ethylidene chloride.	Ethylene chloride.
$C_2H_4 . Cl_2$	$C_2H_4 . Cl_2$"

After having mentioned some other instances, he says: "It is obvious that all cases of isomerism which have so far found no explanation, will, eventually, when the respective substances have been more exactly investigated, be arranged under the heads of polymerism or metamerism; *i.e.* the cause of their difference must depend on a different molecular weight, or on a difference in the relation of the atoms within the molecule."

As examples of isomerism, *i.e.* difference of properties accompanying identity of composition, must be reckoned also, those bodies which, whilst showing an exact correspondence in most of their properties and especially in their essential *chemical* properties, exhibit material differences in their *physical* properties.

To these belong bodies which exist in different optical modifications, as the different modifications of tartaric acid, malic acid, etc., one modification turning the plane of polarised light to the right, and the other to the left.

VIII

Isomeric paraffins—Primary, secondary, and tertiary alcohols—Metameric ethers and esters—Unsaturated compounds.

WE will now compare the views just stated with those resulting from the application of the law of the linking of the atoms, selecting as the most simple example the paraffins.

Their initial member, marsh-gas or methane, CH_4, exists only in one form, and, according to the law, no other is possible. The second member, or ethane, C_2H_6, was believed for a long time to exist in two isomeric modifications. One of them was obtained by Kolbe in the electrolysis of acetic acid, and by Frankland on heating methyl iodide with zinc. The hydrocarbon thus produced was first regarded as the free radical *methyl*, CH_3, and after it was found that, according to Avogadro's law, its molecular formula must be doubled, it was called *dimethyl*. The second hydrocarbon was obtained by Frankland on heating ethyl iodide with zinc and water. He called it *hydride of ethyl*.

These bodies were represented by the following formulæ:—

$$\text{Dimethyl, } \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\} \qquad \text{Ethyl hydride, } \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}$$

Kekulé described these and other supposed isomeric hydrocarbons without attempting to explain their isomerism. In order to do this, the assumption was made subsequently, that the four combining units of carbon had not the same value. But Crum Brown showed that this hypothesis could not be maintained. Butlerow, in endeavouring to explain the isomerism of these bodies, argued that in dimethyl the two carbon atoms were united by two combining units of the same kind, which he called secondary affinities, each being the combining unit, which in methyl iodide, CH_3I, is saturated with iodine. In ethyl hydride the carbon atoms were linked together in the same way as in other ethyl compounds and therefore probably as in the acetyl compounds to which methyl cyanide or acetonitrile, $CH_3 . CN$, belongs. One combining unit was, therefore, that of methyl, and the other that of cyanogen, which must be different. Butlerow called it a primary affinity. In dimethyl, therefore, the carbon atoms were kept together by two secondary affinities, and in ethyl hydride by a secondary and a primary one.

"But by carrying this argument a little further, we arrive," says Crum Brown, "at an absurdity; thus the carbon radical of acetic acid, $CH_3 . CO_2H$, is the same as that of oxyacetic acid, $CH_2(OH)CO_2H$, and that again is the same as the carbon radical of oxalic acid, $CO(OH)CO . OH$, and therefore that of oxalic nitril or cyanogen gas, $CN.CN$. In cyanogen gas, however, we have the two carbon atoms united to by two primary affinities; but we have before proved that in the acetic acid series they are united by a primary affinity of the one to a secondary of the other. It is obvious, then, that at least one of our assumptions is false."[1]

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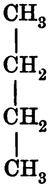
[1] *Trans. Roy. Soc. Edin.* 23, 707.

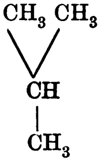
At the same time it was proved that not only the physical but also the chemical properties of dimethyl and ethyl hydride were identical, both being converted by chlorine into ethyl chloride.[1] Since that time many other proofs of the identity of the four combining units of carbon have been found.

If this be correct, the next member in the series, propane, C_3H_8, can only exist in one form, the following, C_4H_{10}, in two, and the next, C_5H_{12}, in three. All these and no more are known—

Butane.

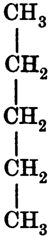


Isobutane.

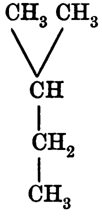


Boiling point + 1° - 17°

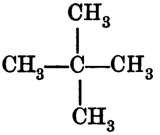
Pentane.



Isopentane.



Tetramethylmethane.



Boiling point 38° 30° 9·5°

If we ascend in the series the number of isomers increases very rapidly, as the following table shows[2] :—

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[1] Schorlemmer, *Proc. Roy. Soc.* 13, 225 ; *Journ. Chem. Soc.*, new series, 2, 263.

[2] Cayley, *Brit. Assoc. Rep.* 1876, 257 ; Hermann, *Ber. deutsch. chem. Ges.* 13, 792.

Number of carbon atoms,	1	2	3	4	5	6	7	8	9	10	11	12	13
Number of paraffins,	1	1	1	2	3	5	9	18	35	75	159	355	802

Of these only a limited number are known, among them being 48 of known constitution. But there can be no doubt that all those predicted by theory can be prepared.

The paraffins show, like other homologous series, how continuous changes in physical properties accompany the gradual increase in molecular complexity. The initial member is methane, CH_4, a gas which at $-164°$ condenses to a liquid, and at a still lower temperature solidifies to a snow-like mass; the highest of known constitution which had been obtained until recently, was pentatriacontane, $C_{35}H_{72}$, a white crystalline body melting at 74·7° and boiling under a diminished pressure only at 331°. We now know a still higher one, hexacontane, $C_{60}H_{122}$, which melts at 101-102°, and decomposes on boiling, even under diminished pressure.

"Each new member is brought into existence by the addition of CH_2 to the molecule of the preceding one, and this quantitative change of the molecule produces every time a qualitatively different body."[1]

If we replace one atom of hydrogen in a paraffin by another element or a radical, we obtain compounds of monad radicals. These radicals have been called the alcohol radicals, because the alcohols were the first known and more closely examined of their compounds. Even to-day they form the usual starting-point for the preparation of other derivatives. The alcohols are hydroxides, and it can be easily

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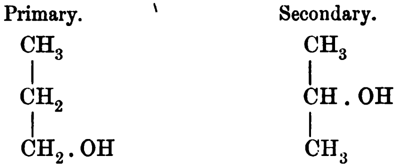
[1] F. Engels, *Herrn Eugen Dühring's Umwälzung der Wissenschaft*, 104.

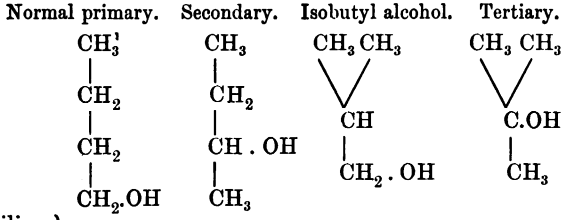
understood that the number of their isomers which our theory predicts is larger than that of the paraffins.

We know only one methyl alcohol, $CH_3 . OH$, one ethyl alcohol, $C_2H_5 . OH$, but two propyl alcohols, $C_3H_7 . OH$, four butyl alcohols, $C_4H_9 . OH$, etc.—

PROPYL ALCOHOLS.



BUTYL ALCOHOLS.



	Normal primary.	Secondary.	Isobutyl alcohol.	Tertiary.
Boiling point	117°	97°	109°	82·5°

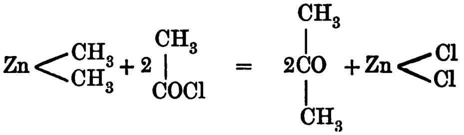
We now know 60 alcohols, and the question arises, What means have we for ascertaining their constitution? We employ the same method as we have used in the case of acetic acid.

Chancel found in 1853 a propyl alcohol in the fusel oil of the spirits obtained from the marc of grapes. This body yields, like ethyl alcohol, an aldehyde, C_3H_6O, and an acid, $C_3H_6O_2$, known before as propionic acid. The acid had been obtained synthetically from ethyl alcohol by converting it into ethyl cyanide or propionitril, $C_2H_5 . CN$, and boiling with potash solution. If we convert this acid into its calcium salt and subject it, mixed with calcium formiate, to dry distillation, the acid is reduced to propionaldehyde—

$$C_2H_5 . CO.OH + HCO . OH = C_2H_5 . COH + CO_2 + H_2O$$

By acting with sodium amalgam on an aqueous solution of this aldehyde it combines with hydrogen, again forming propyl alcohol, to which consequently we have to ascribe the constitution expressed by the first formula.

The second propyl alcohol was obtained by Friedel from acetone or dimethyl ketone, C_3H_6O, which is isomeric with propyl aldehyde.[1] This body is formed by the dry distillation of acetates, and is mentioned by Libavius, who stated that on distilling sugar of lead its quintessence was obtained. Acetone is also produced by passing the vapour of acetic acid through a red-hot tube. According to Williamson it was methyl acetyl, $CH_3 . C_2H_3O$, this formula being afterwards resolved into $CH_3 . CO . CH_3$. This constitution was confirmed by Freund, who obtained acetone by the action of zinc methide on acetyl chloride—



$$\mathrm{Zn}{<}\begin{matrix}CH_3\\CH_3\end{matrix} + 2\begin{matrix}CH_3\\|\\COCl\end{matrix} = 2\begin{matrix}CH_3\\|\\CO\\|\\CH_3\end{matrix} + \mathrm{Zn}{<}\begin{matrix}Cl\\Cl\end{matrix}$$

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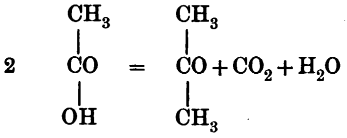
[1] Liebig derived the term aldehyde from *alcohol dehydrogenatum*, because aldehydes are obtained from the alcohols by the abstraction of two atoms of hydrogen. But usually the aldehydes are called after the acids. Thus we say acetaldehyde, propionaldehyde instead of ethyl aldehyde, propyl aldehyde, etc. The International Congress of Chemistry in Paris has, however, proposed that in future the latter nomenclature should be employed.

Its formation from acetic acid is also easily explained—



$$2\ \begin{array}{c}CH_3\\ |\\ CO\\ |\\ OH\end{array} = \begin{array}{c}CH_3\\ |\\ CO\\ |\\ CH_3\end{array} + CO_2 + H_2O$$

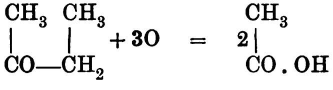
By acting with sodium amalgam on its aqueous solution acetone is converted into secondary propyl alcohol. This on oxidation again yields acetone, which by further oxidation is resolved into acetic acid and formic acid, the latter being partially burnt to carbon dioxide and water.

The first butyl alcohol was discovered in 1852 by Wurtz. It occurs together with propyl alcohol and other alcohols in different kinds of fusel oil. On oxidation it yields an aldehyde and an acid, which was believed to be identical with the butyric acid found in butter and easily obtained also by a peculiar fermentation of sugar. At that time the existence of isomeric alcohols or acids was not in the least suspected, and butyl alcohol was regarded as the true homologue of the three first members of the series. Yet it seemed strange that it should boil at the low temperature of 108-109°. Hermann Kopp. had found that in the homolgous series of the alcohols the boiling point rises about 19° with each increment of CH_2; consequently as ethyl alcohol boils at 78·4°, propyl alcohol at 97°, the boiling point of butyl alcohol ought to have been about 116°.

Now Erlenmeyer, as well as Markownikow, found in 1865 that the acid obtained by the oxidation of this alcohol is not identical with common butyric acid. They called it, therefore, isobutyric acid, and obtained it synthetically by heating secondary propyl iodide with potassium cyanide and boiling the isobutyronitrile, $(CH_3)_2CH.CN$, thus formed with potash. Thus the constitution of isobutyl alcohol, as it was now called, was established.

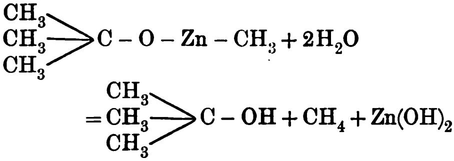
A further proof was found by Duppa and Frankland, who obtained isobutyric acid by replacing two atoms of hydrogen in acetic acid by methyl, whilst by substituting ethyl for one atom of hydrogen they obtained common butyric acid, which is also a product of oxidation of the normal primary alcohol. This Lieben and Rossi had obtained synthetically from butyric acid by the same method as they employed for reducing propionic acid to propyl alcohol.

A third butyl alcohol was discovered in 1863 by de Luynes. He obtained it from erythrite, $C_4H_6(OH)_4$, a body nearly related to mannite, by a reaction which did not give any clue to its constitution. But as it behaved very similarly to secondary propyl alcohol, yielding on oxidation ethyl-methyl ketone, $C_2H_5.CO.CH_3$, its constitution did not appear open to doubt. This ketone has been obtained synthetically from acetyl chloride and zinc ethide $(C_2H_5)_2Zn$; it combines with hydrogen to form secondary butyl alcohol, and by oxidation it is resolved into two molecules of acetic acid—



$$\begin{array}{ll}CH_3 & CH_3\\ | & |\\ CO- & CH_2\end{array} + 3O = 2\begin{array}{l}CH_3\\ |\\ CO.OH\end{array}$$

Tertiary butyl alcohol was discovered in 1863 by Butlerow, who found that by adding an excess of zinc methide to acetyl chloride, a crystalline body was gradually formed, which was decomposed by water with the formation of tertiary butyl alcohol, methane, and zinc hydroxide. In this reaction acetone is first formed; it then combines with zinc methide, and the body thus formed is acted upon by water as follows:—



$$(CH_3)_3 \equiv C - O - Zn - CH_3 + 2H_2O = (CH_3)_3 \equiv C - OH + CH_4 + Zn(OH)_2$$

That the alcohol has this constitution has since been proved in different ways. On oxidation it yields neither an aldehyde nor a ketone, but is resolved into acetic acid and formic acid or the oxidation products of the latter.

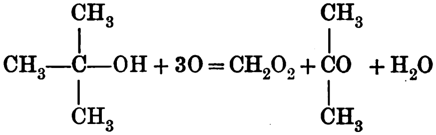
These examples show how we ascertain the constitution of the alcohols. They are divided into three distinct groups: *Primary*, *Secondary*, and *Tertiary*. In order to find out to which group an alcohol belongs, we have only to examine its products of oxidation.

A primary alcohol yields first an aldehyde, which is easily oxidised further to an acid containing in its molecule the same number of carbon atoms as the alcohol.

A secondary alcohol yields first a ketone, which is less easily attacked by oxidising agents than an aldehyde, and by further oxidation is resolved into two fragments, one alcohol radical remaining combined with the carbonyl and yielding a fatty acid, whilst the second alcohol radical is oxidised in the same way as the corresponding alcohol would be.

A tertiary alcohol is broken up by oxidation into three fragments; one of the alcohol radicals remains in combination with the carbon atom, which kept the group together, while the two other alcohol radicals yield the same oxidation products as the corresponding alcohols.

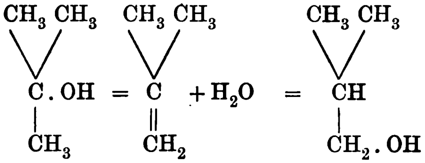
These are, however, only the final products. Butlerow found that tertiary butyl alcohol yields some acetone besides acetic acid and carbon dioxide. This is easily accounted for by the alcohol being first oxidised to formic acid and acetone—



$$CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}OH + 3O = CH_2O_2 + \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CO}} + H_2O$$

These, by further oxidation, are then converted into acetic acid, water, and carbon dioxide.

But, strange to say, Butlerow also obtained a small quantity of isobutyric acid, and found that other tertiary alcohols behaved in a similar way, yielding a minimal quantity of an acid containing the same number of carbon atoms as the alcohol. For this he found an explanation: tertiary alcohols are easily resolved into water and an olefine, whilst, under certain conditions, the latter combines again with water to form the tertiary alcohol; but at the same time a small quantity of a primary alcohol may be produced, thus—



$$\underset{\underset{CH_3}{|}}{\overset{CH_3\ CH_3}{\overset{\diagdown\ \diagup}{C.OH}}} = \underset{\underset{CH_2}{\|}}{\overset{CH_3\ CH_3}{\overset{\diagdown\ \diagup}{C}}} + H_2O = \underset{\underset{CH_2.OH}{|}}{\overset{CH_3\ CH_3}{\overset{\diagdown\ \diagup}{CH}}}$$

The physical properties of carbon compounds may also be used for the determination of their constitution. It has been found, for example, that normal compounds,—by which we mean such as contain a single chain of carbon atoms,—always boil at a higher temperature than their isomers.

In the tar from cannel coal and in American petroleum a series of paraffins was found, differing from their previously known isomers by having a higher boiling point. The constitution of the latter was not then known, but was cleared up a short time afterwards, when it was found that they contain the group $(CH_3)_2CH$—to which a single chain of carbon atoms is attached. From this the conclusion was drawn that the hydrocarbons from tar and petroleum must have a more simple constitution, and that they were normal compounds. By further investigation this view was proved to be correct.

We find, further, that a primary alcohol always boils at a higher temperature than an isomeric secondary one, and the boiling point of the latter is above that of a tertiary alcohol.

Compounds having the same composition and the same molecular weight we call, if all the carbon atoms are linked together, *Isomers proper* (*Isomere im engeren Sinne*).

The word *metameric* is applied to compounds like ethers or amines where we have identity of molecular formula produced by the grouping of different radicals round the atom of some polyvalent element other than carbon. The carbon atoms in metameric bodies are therefore not in an uninterrupted chain. Propyl alcohol and isopropyl alcohol are isomers, whilst ethyl ether, $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$ and methyl propyl ether, $\left.\begin{matrix}CH_3\\C_3H_7\end{matrix}\right\}O$ are metamers.

Naumann has shown that in the case of isomeric alcohols and metameric ethers the boiling point is the lower the nearer the oxygen is placed to the middle of the chain.

		Boiling Point.
Primary butyl alcohol .	$CH_3.CH_2.CH_2.CH_2.OH$	116°
Secondary butyl alcohol	$CH_3.CH_2.CH(OH)CH_3$	97°
Methylpropyl ether .	$CH_3.CH_2.CH.O.CH_3$	50°
Diethyl ether . .	$CH_3.CH_2.O.CH_2.CH_3$	35·5°

The paraffins and their derivatives have also been called *saturated* compounds, while those derived from them by the abstraction of hydrogen have been named *unsaturated*, because they combine additively with the elements of the chlorine group and their hydracids, and with other molecules.

The physical properties of the olefines are almost the same as those of the corresponding paraffins; they have the same specific gravity, the same boiling points, etc. But nothing is easier than to distinguish an olefine from a paraffin. On adding bromine to the former the colour disappears at once, heat being evolved and a dibromide formed by *addition*; whilst when we mix a paraffin with bromine a change only sets in slowly when the mixture is exposed to light, hydrobromic acid being evolved and *substitution* taking place.

To explain the constitution of the olefines three hypotheses have been proposed:

1. They contain a carbon atom with free combining units.
2. They contain a dyad carbon atom.
3. Two carbon atoms are linked together by two combining units of each.

The first hypothesis had, some years ago, a number of adherents. Lothar Meyer, in discussing it, says:

"It offers in nowise a philosophical difficulty; it cannot be astonishing that, under certain conditions, one or more affinities remain unsaturated; on the contrary, it would be wonderful if such free affinities did not exist.

"The assumption of non-saturated affinities is indeed unavoidable for certain compounds, such as nitric oxide, NO, carbonic oxide, CO, the vapour of mercury, Hg, of cadmium, Cd, of calomel, HgCl. Moreover, we require it for the explanation of the two different substances, C_2H_3Cl, one of them having been obtained by Regnault from elayl, and the other by Harnitz-Harnitzky from phosgene and aldehyde."[1]

According to this hypothesis the most simple olefine, ethylene or elayl, as it was formerly called, ought to exist in two isomeric forms—

$$\begin{array}{l} CH_3 \\ | \\ CH= \end{array} \qquad\qquad \begin{array}{l} CH_2- \\ | \\ CH_2- \end{array}$$

Experiments made by Meyer and Tollens for the purpose of obtaining a second ethylene failed. But the existence of two monochlorethylenes appeared to be indubitable. One, called *vinyl chloride*, had been prepared by Regnault from ethylene dichloride, which, by the action of hot alcoholic potash loses the elements of hydrochloric acid—

$$C_2H_4Cl_2 + KOH = C_2H_3Cl + KCl + H_2O$$

The second was formed, according to Harnitz-

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[1] *Ann. Chem. Pharm.* 139, 285.

Harnitzky, who named it *chloracetene*, by the action of carbonyl chloride on aldehyde—

$$C_2H_4O + COCl_2 = C_2H_3Cl + HCl + CO_2$$

The existence of these two bodies was of the highest interest, because it could only be explained by the hypothesis of free-combining units or dyad carbon, which, if found true in such a simple case, would hold good in the more complicated cases.

Kekulé and Zincke therefore repeated Harnitzky's experiments. They said that from their theoretical standpoint the existence of chloracetene did not appear to be very probable, and they therefore sought to make its personal acquaintance:

"Four possibilities presented themselves:—

"1. Chloracetene is really isomeric with vinyl chloride, and has the same molecular weight.

"2. The two compounds are perhaps polymeric, and chloracetene forms, by a breaking up of its molecule, a lighter vapour.

"3. Vinyl chloride has perhaps not been obtained quite pure, and is in the pure state identical with chloracetene.

"4. It is also possible that the statements about chloracetene are based on error, and many even on fancy (*Schwindel*)."

They found, as the result of their research, that Regnault's statements were perfectly correct, and that chloracetene possessed, besides other remarkable properties, that of non-existence! It was found to be a mixture of carbonyl chloride, aldehyde, and paraldehyde.[1]

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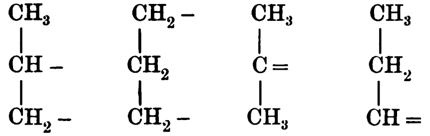
[1] *Ber. deutsch. chem. Ges.* 3, 129 and 136.

According to the hypothesis of dyad carbon, only one ethylene, $CH_3 - CH$, can exist. But it can be easily proved that ethylene has not this constitution. When we heat ethylene dibromide, $C_2H_4Br_2$, with water under pressure, we get ethylene alcohol or glycol, $C_2H_4(OH)_2$, which by the action of hydrochloric acid is converted into ethylene chlorhydrin, $C_2H_4(OH)Cl$, and on oxidising this, we obtain chloracetic acid, $CH_2Cl . CO . OH$. From this it appears that the chlorhydrate is chlorethyl alcohol, $CH_2Cl . CH_2 . OH$, and that the radical ethylene has the constitution $CH_2 - CH_2$.

The next homologue of ethylene is propylene, C_3H_6, which in accordance with the hypothesis of free combining units ought to exist in four modifications—



Methyl-ethylene. $\begin{matrix} CH_3 \\ | \\ CH - \\ | \\ CH_2 - \end{matrix}$ Trimethylene. $\begin{matrix} CH_2 - \\ | \\ CH_2 \\ | \\ CH_2 - \end{matrix}$ Dimethyl-methylene. $\begin{matrix} CH_3 \\ | \\ C = \\ | \\ CH_3 \end{matrix}$ Ethyl-methylene. $\begin{matrix} CH_3 \\ | \\ CH_2 \\ | \\ CH = \end{matrix}$

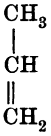
In common propylene the atoms are arranged as shown by the first formula. This is proved by the fact that we can easily convert the hydrocarbon into propylene alcohol or propylene glycol and lactic acid (p. 123).

We know, however, the four dichlorides, $C_3H_6Cl_2$, and dibromides, $C_3H_6Br_2$, of the above radicals. As these, when heated with sodium, yield one and the same propylene, the conclusion was drawn that only one propylene existed. This can be obtained by heating primary or secondary propyl iodide with alcoholic potash, and it combines again with hydriodic acid to form the secondary iodide, proving again that it has the constitution assigned to it.

More recently, however, a second propylene has been discovered. It was found that when trimethylene bromide, $CH_2Br.CH_2.CH_2Br$, was heated not too strongly with sodium, it yielded a hydrocarbon, which combined with bromine again to form trimethylene dibromide, and with hydriodic acid to form primary propyl iodide.

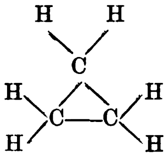
These and similar cases of isomerism can be explained without the hypothesis of free combining units or dyad carbon. In ethylene and common propylene two carbon atoms are linked together by two combining units of each—

$$\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array}$$



$$\begin{array}{c} CH_3 \\ | \\ CH \\ \| \\ CH_2 \end{array}$$

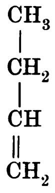
This double linking is easily resolved into the single one by the action of bromine, hydriodic acid, etc. The isomeric propylene or trimethylene differs from its isomer not only in yielding isomeric compounds, but also in these not being formed so readily, bromine and hydriodic acid combining with it more slowly than with common propylene. From this it would appear that trimethylene does not contain free combining units, and we therefore assume that its carbon atoms form a closed chain—



We have already seen that four butyl iodides, C_4H_9I are known. On heating these with caustic potash we obtain only three butylenes, C_4H_8. One of these is furnished by the primary iodide, the second by the secondary iodide, and both olefines combine again with hydriodic acid to form the secondary iodide. The third butylene is obtained from isobutyl iodide, and from tertiary butyl iodide; by combining it with hydriodic acid we again get the tertiary compound.

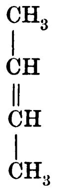
The butylenes have, therefore, the following constitution:—

α-Butylene.



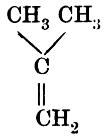
$CH_3-CH_2-CH=CH_2$

β-Butylene.



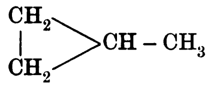
$CH_3-CH=CH-CH_3$

Isobutylene.

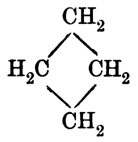


Besides these the following can exist, but have not yet been obtained:—

Methyltrimethylene.



Tetramethylene.



By abstracting from the olefines two atoms of hydrogen, we get the series C_nH_{2n-2}, from which we may pass to that of C_nH_{2n-4}, etc. These hydrocarbons contain several double or triple linkings; they combine like the olefines with the elements of the chlorine group and their hydracids, being finally converted into bodies of the paraffin type. Thus dipropinyl, $CH \vdots C . CH_2 . CH_2 . C \vdots CH$, takes up eight atoms of bromine and yields an octobromide, $C_6H_6Br_8$.

The paraffins and their derivatives form a large group called the group of the *fatty bodies* or *aliphatic compounds* (ἄλειφαρ, fat). This name arose from the fact that the first members of the group which received careful study were the fatty acids. The compounds derived from them by the abstraction of hydrogen are still often called *unsaturated bodies*, whilst Kekulé designates them "wasserstoffärmere Verbindungen."

IX

Aromatic compounds—Kekulé's hypothesis—Disubstitution products of benzene — Ladenburg's views —Tautomeric formulæ —The arrangement of atoms in space—Geometrical isomerism—Kolbe's views.

THE name *aromatic compounds* has been given to a second large class of carbon compounds, because most of those which occur in nature are found in essential oils, balsams, and other bodies having an aromatic odour. They differ from the aliphatic compounds in containing relatively more carbon; hence Kekulé called them "kohlenstoffreichere Verbinungen."

No expression of opinion is to be found respecting their constitution until 1865, when Kekulé proposed a theory that shed an unexpected light on this hitherto somewhat neglected group. This theory has had such an influence on the development of theoretical and technical chemistry, that on the 11th March 1890, the 25th anniversary of its birth was celebrated by a great chemical *fête,* at which all classes and nationalities of chemists were represented.[1]

"If we wish to give an account of the atomic

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[1] Kekulé, *Bull. Soc. chim.* 1865, 1, 98; *Ann. Chem. Pharm.* 137, 129; see alsc *Ber. deutsch. chem. Ges.* 23, 1265.

constitution of the aromatic compounds, we are bound to explain the following facts:—

" 1. All aromatic compounds, even the most simple, are relatively richer in carbon than the corresponding compounds in the class of fatty bodies.

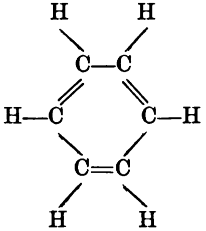
" 2. Among the aromatic compounds, as well as among the fatty bodies, a large number of homologous substances exist.

" 3. The most simple aromatic compounds contain at least six atoms of carbon.

" 4. All the derivatives of aromatic substances exhibit a certain family likeness; they all belong to the group of 'aromatic compounds.' In cases where more vigorous reactions take place, a portion of the carbon is often eliminated, but the chief product contains at least six atoms of carbon. The decomposition stops with the formation of these products, unless the organic group be completely destroyed.

" These facts justify the supposition that all aromatic compounds contain a common group, or, we may say, a common *nucleus*, consisting of six atoms of carbon. Within this *nucleus* a more intimate combination of the carbon atoms takes place; they are more compactly placed together, and this is the cause of the aromatic bodies being relatively rich in carbon. Other carbon atoms can be joined to this *nucleus* in the same way and according to the same law, as in the case of the group of fatty bodies, and in this way the existence of homologous compounds is explained."

According to Kekulè, the six atoms of carbon forming the aromatic *nucleus* are alternately linked together by one and by two combining units to form a ring or a closed chain containing six free combining units. If these be saturated with hydrogen we obtain benzol or benzene, C_6H_6, which is the most simple aromatic compound, and has the following constitution:—

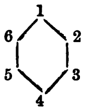


Benzene may be called the marsh-gas of the aromatic group, inasmuch as all the other compounds are derived from it by the substitution of elements or radicals for hydrogen.

Kekulé's formula accounts also for the following facts:—

1. Isomeric mono-substitution products of benzene do not exist, the six hydrogen atoms of this hydrocarbon being equivalent.

2. On replacing two atoms of hydrogen by other elements, or by radicals, which are called *side chains*, we can obtain three isomeric compounds, irrespective of whether the substituting groups are all the same or are different. This has been proved by experience, and the isomerism is readily explained by the substituents taking up different positions in the ring. If we represent benzene as a hexagon, and number the six corners which we suppose to be occupied by the carbon atoms, it is easily seen that three dibromobenzenes, $C_6H_4Br_2$, can exist—



the bromine atoms occupying the following positions:—

1 : 2
1 : 3
1 : 4

Every other arrangement is identical with one of these.

3. Whilst benzene ordinarily yields substitution products with chlorine or bromine, it can, under certain conditions, form additive products, and combine with two, four, or six atoms of these elements, but not with more.

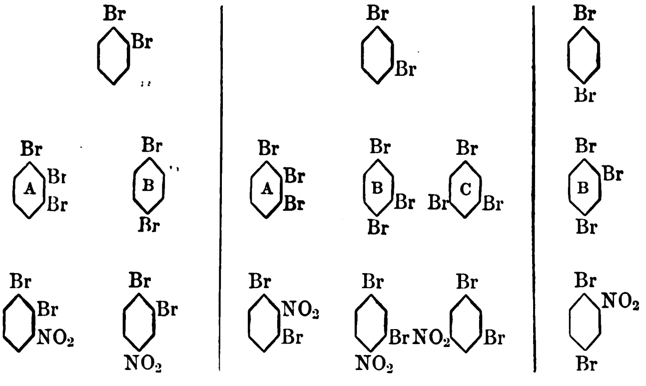
On propounding his theory, Kekulé said: "Some chemists appear to be of opinion that benzene and its homologues were derived from the hydrocarbons of the fatty group by a simple abstraction of hydrogen, by which the carbon atoms were pushed more closely together. I cannot share this view, and I believe that a hydrocarbon of the formula C_6H_6, which may perhaps be obtained by abstracting hydrogen from C_6H_{12} . . . will be isomeric, but not identical with benzene."

This hydrocarbon has since been discovered; it is the dipropinyl which has already been mentioned. It was then stated that it readily forms an octobromide. Benzene behaves quite differently; it does not combine readily with bromine, and we cannot add more than six atoms of bromine or chlorine. The formation of these additive products is quite analogous to the formation of the additive compound of ethylene, the double linking of the carbon atoms being resolved into the single one; but the ring remains unbroken. By the action of alkalis on ethylene dibromide, $C_2H_4Br_2$, we obtain monobromethylene, C_2H_3Br, and by the same reaction we convert benzene hexabromide, $C_6H_6Br_6$, into tribromobenzene, $C_6H_3Br_3$.

As soon as the fact was established that benzene could yield three isomeric di-substitution products, chemists endeavoured to find out the relative position of the substituents. The first attempts at such an *orientation* were not quite successful, but by and by methods were found by which the constitution of the di-substitution products was firmly established. We will first describe Körner's method.

Starting with the supposition of the equivalence of the six hydrogen atoms of benzene, he used for the orientation a method based on the following principles:—

An *ortho* compound (1 : 2) with identical substituents can, by replacement of a third hydrogen atom, yield two triderivatives. Under the same conditions a *meta* compound (1 : 3) can give rise to three triderivatives, and a *para* compound (1 : 4) only one. If the new substituent be identical with those already present, only three trisubstitution products will be formed; if not, six will be obtained. This is shown by the following diagram:—



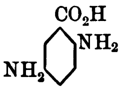
From this it follows that in a dibromobenzene, which yields three tribromobenzenes or three nitrodibromobenzenes, the bromine atoms occupy the positions 1 : 3.

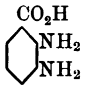
Ortho-dibromobenzene with the position 1 : 2 gives only two tribromobenzenes and only two nitrodibromobenzenes.

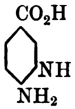
Finally paradibromobenzene (1 : 4) yields only one tribromobenzene and one nitrodibromobenzene.

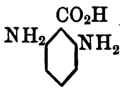
The constitution of a large number of other disubstitution products was established by Körner[1] in a similar manner.

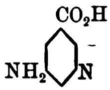
Almost at the same time Peter Griess made use of this principle in order to ascertain the constitution of the three diamidobenzenes, $C_6H_4(NH_2)_2$, which he prepared by the abstraction of carbon dioxide from the six diamidobenzoic acids, $C_6H_3(NH_2)_2CO_2H$—

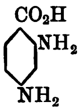












From the first of these he obtained paradiamidobenzene melting at 147°; the two following yielded orthodiamidobenzene, which melts at 99°, and the last three gave metadiamidobenzene, melting at 63°.

In the same way the constitution of a large number

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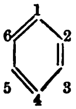
[1] *Gaz. chim. ital.* 4, 305 ; *Journ. chem. Soc.* 1876, 1, 204.

of other derivatives of benzene, and its homologues has been ascertained.

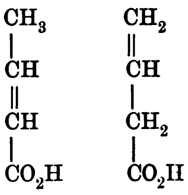
Thus salicylic acid was found to be orthohydroxybenzoic acid, $C_6H_4(OH)CO_2H$; oxybenzoic acid was recognised as the meta compound, and we know also the third modification or parahydroxybenzoic acid.

Ladenburg, however, raised an objection to Kekulé's formula, maintaining that four isomeric di-substitution products ought to exist, as the position 1 : 2 was not identical with 1 : 6 [1]—



Two substituents in the position 1 : 2 are combined with two carbon atoms which are linked together by only one combining unit of each atom, whilst when in the position 1 : 6 they are united to two doubly-linked carbon atoms. The question whether the position 1 : 3 = 1 : 5 appeared to be more simple, and might be answered in the affirmative.

If, says Ladenburg, the positions 1 : 2 and 1 : 6 were identical, it ought also to be the case for the two crotonic acids—



$$\begin{array}{l} CH_3 \\ | \\ CH \\ \| \\ CH \\ | \\ CO_2H \end{array} \qquad \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2 \\ | \\ CO_2H \end{array}$$

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[1] *Ber. deutsch. chem, Ges.* 7, 1226.

But the isomerism of these two acids depends not merely on the different arrangement of the linkage, but also on a different distribution of the hydrogen.

V. Meyer opposed Ladenburg, pointing out that the difference between the positions 1 : 2 and 1 : 6 was not caused by a different position of the atoms, but only by a different arrangement of the linkage, and was, therefore, of such a subtle nature, that it appeared doubtful whether so nice a distinction would have any marked influence on the properties of the compound.[1]

Kekulé took a different view; the possible difference of the di-derivatives 1 : 2 and 1 : 6 is too much insisted upon; it takes its origin rather from the form employed than from the ideas of which the form affords only an imperfect representation. To show that no such difference exists, Kekulé brought forward the following hypothesis:—

"The atoms in the systems which we call molecules must be considered to be continually in motion. This view has often been expressed by physicists and chemists, and I have discussed it already in the first part of my handbook. Hitherto no explanation, as to the form of this intramolecular motion, has been given as far as I know. Chemistry must, at all events, bring forward the claim, that such a mechanical hypothesis accounts for the law of the linking of the atoms. A planetary motion seems, therefore, not admissible, the movement must be of such a kind that all the atoms forming the system retain the same relative arrangement—in other words, that they return to a mean position of equilibrium. If we now select from the numerous conceptions,

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[1] *Ann. Chem. Pharm.* 156, 265; 159, 24.

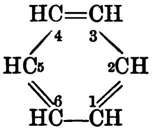
which may be formed, that which gives the most complete account of the chemical claims and which the most closely coincides with the hypothesis of our modern physicists as to the mode of the motion of molecules, the following assumption will appear the most probable:—

"The simple atoms of the system approach each other in what may be considered a straight line, and rebound as elastic bodies. What we call valency would then have a mechanical meaning. Valency is the number of contacts experienced by one atom on the part of other atoms in the unit of time. In the same time that the monad atoms of a diatomic molecule strike each other once, the dyad atoms of a diatomic molecule come into contact with each other twice, the temperature in both cases being the same. In a molecule consisting of one dyad and two monads, the number of contacts, under the same conditions, in the unit of time, is two for the dyad and one for each monad atom.

"If two atoms of tetrad carbon are linked together by one combining unit of each, they strike against each other once in the unit of time, or in the same time in which monad hydrogen makes a complete vibration. During this time they encounter three other atoms. Carbon atoms which we call doubly linked come in contact twice in the unit of time and experience during the same time two contacts with other atoms, etc.

"If we now apply these views to benzene, the formula which I have proposed appears as an expression of the following conception. Each carbon atom strikes against two others in the unit of time, once against one and twice against the other. In the same unit of time it comes once in contact with hydrogen and completes one vibration.

"If we now represent benzene by the known hexagon formula and fix our attention on one of the carbon atoms, for instance that marked by 1—



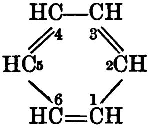
we can express the contacts which it experiences in the first unit of time by

(1.) 2, 6, *h*, 2.

"In this formula *h* stands for hydrogen. In the second unit of time that carbon atom which has just encountered No. 2, turns next to No. 6. Its contacts during the second unit of time are—

(2.) 6, 2, *h*, 6.

"While the contacts of the first unit of time are expressed by the above formula, those during the second unit are represented by—



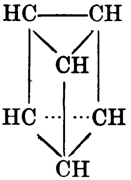
"The same carbon atom is, therefore, during the first unit of time in double linkage with one of the adjoining carbon atoms and in the second unit of time with the other.

"The most simple mean of all the contacts of one carbon atom is found from the sum of the contacts during the two first units of time, which then repeat themselves periodically. This mean is, therefore—

2, 6, *h*, 2, 6, 2, *h*, 6 ;

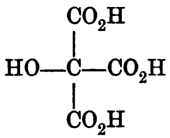
and we see now that each carbon atom strikes against the two others, with which it is directly combined, an equal number of times, or it bears the same relation to each of its neighbours. The ordinary formula for benzene only represents the contacts made during the first unit of time, or only one phase, and thus the view has sprung up that the di-derivatives with the positions 1, 2 and 1, 6 must be necessarily different. If the above hypothesis or a similar one may be considered to be correct, it follows that this difference is only apparent, not real."

According to Ladenburg we can explain the constitution of benzene most simply by assuming that the carbon atoms occupy the corners of a triangular prism—



This formula explains the existence of the three di-substitution products, of the additive products, etc., as readily as that of Kekulé. It found further support in the following facts:—

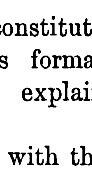
When protocatechuic acid, $C_6H_3(OH)_2CO_2H$, or catechol, $C_6H_4(OH)_2$, is acted upon by nitrous acid a compound is formed which has been called *carboxytartronic acid,* $C_4H_4O_7$, because it is very easily resolved into carbon dioxide and tartronic acid, $CH(OH)(CO_2H)_2$. Hence the following constitution was assigned to it:—



$$\begin{array}{c} CO_2H \\ | \\ HO{-}C{-}CO_2H \\ | \\ CO_2H \end{array}$$

It would, therefore, contain one carbon atom, combined with three others, and as it is obtained by a simple reaction from simple derivatives of benzene, it appeared highly probable that the same mode of linking would be found in the aromatic nucleus, and this pointed to the prism formula.

Kekulé found, however, that carboxytartronic acid has the formula $C_4H_6O_8$, and that it is not a tribasic but a bibasic acid, which by reduction is converted into one of the tartaric acids. He then obtained it from the so-called nitro-tartaric acid, $C_2H_2(ONO_2)_2(CO_2H)_2$, and showed that it is dioxytartaric acid—



$$\begin{array}{l} CO_2H \\ | \\ C{<}\begin{smallmatrix}OH\\OH\end{smallmatrix} \\ | \\ C{<}\begin{smallmatrix}OH\\OH\end{smallmatrix} \\ | \\ CO_2H \end{array}$$

Now, although its constitution does not contradict the prism formula, its formation from catechol is certainly more easily explained by the hexagon formula.

The same is the case with the formation of *trichloro-*

phenomalic acid, $C_6H_7Cl_3O_5$, which Carius obtained by the action of sulphuric acid and potassium chlorate on benzene—

$$C_6H_6 + 3ClO_2H = C_6H_7Cl_3O_5 + H_2O$$

By heating it with baryta water it is converted into phenaconic acid—

$$C_6H_7Cl_3O_5 + H_2O = C_6H_6O_6 + 3HCl$$

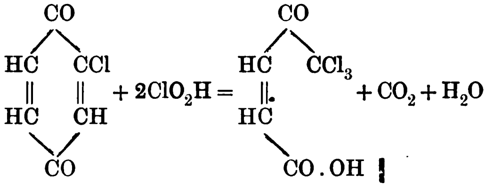
This when heated with hydriodic acid yielded succinic acid, $C_4H_6O_4$. To explain this remarkable reaction, Carius assumed that a polymeric change took place. He found subsequently that phenaconic acid was identical with fumaric acid, $C_4H_4O_4$. This explained the formation of succinic acid, but trichlorophenomalic acid remained a mysterious body; its decomposition into hydrochloric acid and fumaric acid was unexplained. Kekulé and Strecker therefore undertook a new investigation of it. In the introduction to their paper they say: "If we are to summarise briefly the result of our critical studies, we may call it, "A Comedy of Errors." Trichlorophenomalic acid is not formed according to the equation which Carius has given, and it has not the formula which he assigned to it. It does not give off hydrochloric acid by treating it with alkalis, nor does it yield fumaric acid; but nevertheless the phenaconic acid of Carius is fumaric acid."

They found that trichlorophenomalic acid is trichloracetylacrylic acid, which, when heated with baryta water is resolved into chloroform and maleïc acid—

$$C_5H_3Cl_3O_3 + H_2O = C_4H_4O_4 + CHCl_3$$

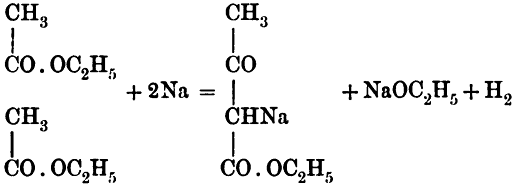
Maleïc acid is isomeric with fumaric acid and easily changes into it, as we shall see later. The last statement of Carius is thus explained.

Trichloracetylacrylic acid is not formed from benzene by a simple reaction; a number of bye-products are obtained at the same time, amongst which are chlorinated quinones. The acid is also produced by the action of chlorous acid on quinone, and its formation is most readily explained by assuming that it is obtained from monochloroquinone in the following way:—



If we endeavour to explain its formation by accepting the prism formula, we meet, say Kekulé and Strecker, not with insurmountable difficulties, but with undeniable improbabilities. "We are first of all obliged to assume that five single linkings of the carbon atoms were loosened, three of them by the carbon atom which is removed, which of course would not be remarkable, but two others in such a way that a normal carbon chain is formed as it exists in trichloracetylacrylic acid. Besides, we have to make the most improbable assumption that from a single carbon linkage a double one would be produced under conditions which would have led us to expect much more probably the loosening of a double linkage."

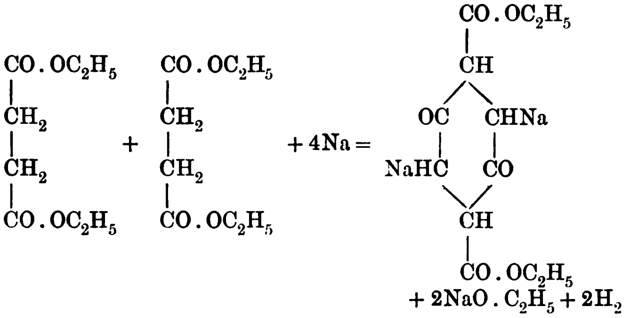
The correctness of the hexagon formula has been further proved by Baeyer. In order to understand his proof we must first mention the formation of a most important compound, of which we shall have to say more subsequently. This body which is called aceto-acetic ester is formed by the action of sodium on ethyl acetate. To explain the reaction two hypotheses have been employed; of these we will mention at present only one. According to this the following reaction takes place:—



$$\begin{array}{l}CH_3\\ |\\ CO.OC_2H_5\\ CH_3\\ |\\ CO.OC_2H_5\end{array} + 2Na = \begin{array}{l}CH_3\\ |\\ CO\\ |\\ CHNa\\ |\\ CO.OC_2H_5\end{array} + NaOC_2H_5 + H_2$$

By treating the product with acetic acid the sodium is replaced by hydrogen, and we obtain the pure compound $CH_3 . CO . CH_2 . CO . OC_2H_5$.

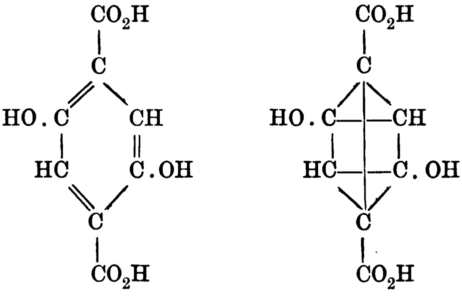
Other esters are acted upon by sodium in a similar way; ethyl succinate yielding the sodium compound of succino-succinic ester—



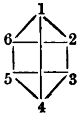
If we treat the product with an acid, we obtain the ester, which is also formed by the action of sodium upon bromaceto-acetic ester, hydrobromic acid being given off.

By oxidation succino-succinic ester is converted into ethyldihydroxyterephthalate, $C_6H_2(OH)_2(CO_2 . C_2H_5)_2$, which is also obtained by treating dibromaceto-acetic ester with sodium. This body has very singular properties, forming either white or green crystals. The latter are formed at a low temperature and change on heating into the former. By alternate cooling and warming a crystal may be changed any number of times into one or other modification, and if this be done quickly it produces an impression as of the crystals being alternately drawn out and pressed together like an accordion, since with the colour the shape also varies.

From the ethyl ester we can obtain the free acid which may be represented either by Kekulé's or by Ladenburg's formula—



The first of these certainly explains its formation more readily than the second; the latter indeed cannot be admitted at all, because on heating the acid it is resolved into carbon dioxide and quinol or paradihydroxybenzene, $C_6H_4(OH)_2$, in which the hydroxyls have the position 1 : 4. If we now number the corners of the prism—

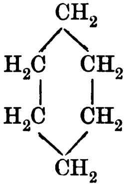


we find by using Körner's method of orientation, that

1 : 2 = Meta
1 : 3 = Ortho
1 : 4 = Para

Consequently, in adopting the prismatic formula we could not, under the circumstances described, obtain a para-compound, but instead orthodihydroxybenzene or catechol would be formed.

From these and other observations Baeyer concludes that the six carbon atoms of benzene are united in a ring, and that the products formed by combining benzene or its derivatives with six atoms of hydrogen or other monad elements are derivatives of hexmethylene, which has the following constitution[1]:—



Of the twenty-four combining units of the carbon atoms in benzene, twelve are employed for forming the ring, six are saturated with hydrogen, and the other six, according to Kekulé, produce the double linking of three pairs of carbon atoms. Now Baeyer found that terephthalic acid, $C_6H_4(CO_2H)_2$, combines with two,

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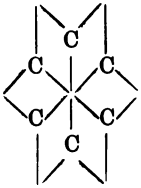
[1] *Ber. deutsch. chem. Ges.* 19, 1803.

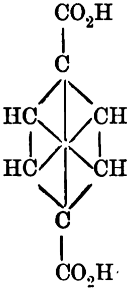
four, or six atoms of hydrogen, the final product being hexhydroterephthalic or hexmethylenedicarboxylic acid, $C_6H_{10}(CO_2H)_2$. This body behaves like a saturated aliphatic compound; it neither combines with bromine in the cold, nor with hydrobromic acid; it is not attacked by an alkaline solution of potassium permanganate. Tetrahydroterephthalic acid, $C_6H_8(CO_2H)_2$, is readily oxidised, and it combines with one molecule of bromine or hydrobromic acid. From this we must conclude that it contains a double linking like the olefines. Dihydroterephthalic acid is still more easily oxidised, and it combines with two molecules of bromine or hydrobromic acid. Consequently it must contain two double linkings; and therefore, if terephthalic acid contained three double linkings, it would readily combine with three molecules of bromine and be a less stable body than the two hydroterephthalic acids. But this is not the case, terephthalic acid being as stable a compound as hexhydroterephthalic acid. Consequently Kekulé's formula appears improbable, and Baeyer has replaced it by one which had previously been suggested by Kekulé in 1866, and according to which the carbon atoms form a symmetrical ring in which the carbon would be trivalent. Kekulé, however, did not insist upon this formula owing to the difficulty of explaining the trivalency of carbon, which had never been observed in the fatty group. This difficulty Baeyer gets over by arranging the atoms in space. It is assumed that the six carbon atoms, in consequence of the attraction of the free bonds turn on the axes formed by the sides of the hexagon in such a way that their direction tends inwards towards the plane of the ring, the six points of attack lying symmetrically within the ring and neutralising each other, so that they are practically unavailable,—in other words carbon is trivalent—



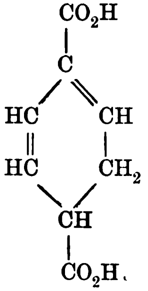
The fourth combining unit of each carbon atom, which is saturated with hydrogen, is supposed to be nearly perpendicular to the plane of the drawing, and thus the hydrogen atoms are situated in a plane parallel with that of the carbon atoms.

In the model two groups of opposing forces are represented, the central bonds tending to draw the atoms towards the middle point, and the peripheral bonds striving to widen out the ring. In benzene these forces are in equilibrium, but as soon as two central bonds become united to hydrogen, the equilibrium is destroyed, and the tension of the peripheral bonds, expanding the ring, causes the four remaining bonds to form a double linking—

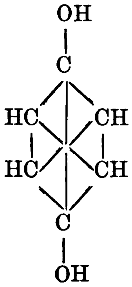
Terephthalic aci

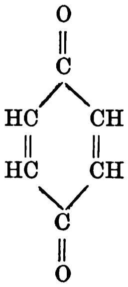


Dihydroterephthalic acid.



The same is seen in the oxidation of quinol, $C_6H_4(OH)_2$, to quinone, $C_6H_4O_2$—

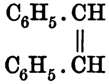




The cause of the passivity of the central bonds we cannot at present explain; whether it depends on the geometrical structure which prevents other atoms from penetrating into the interior, or on a more dense state of ether in the centre of the ring, must be left undecided.[1]

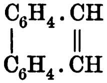
Further researches by Baeyer have shown that the unsaturated hydroterephthalic acids, or those containing double linkings, must be classed among the unsaturated aliphatic. compounds, and that all the isomeric forms which theory predicts can be prepared. At the same time he has found facts which have induced him to give up his opposition to Kekulé's formula. The following compounds have an analogous constitution:—

Stilbene.



$$\begin{array}{l} C_6H_5.CH \\ \quad\quad\ \| \\ C_6H_5.CH \end{array}$$

Phenanthrene.



$$\begin{array}{l} C_6H_4.CH \\ \ \ | \quad\ \ \| \\ C_6H_4.CH \end{array}$$

Now stilbene is at once oxidised by potassium per-

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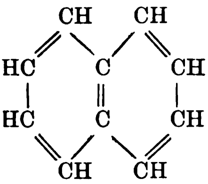
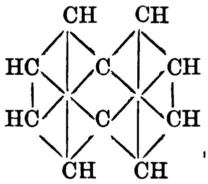
[1] *Ann. Chem. Pharm.* 245, 103.

manganate in the cold; phenanthrene is not attacked—a fact which can be only accounted for by the closing of the ring. But as the action of potassium permanganate on the hydrophthalic acids proves that the double linking in closed chains is as sensitive towards this oxidising agent as in open ones, it follows that the stability of phenanthrene does not solely depend on the closing of the ring, but also on some other unknown cause—the same probably that protects in the same way the double linking in benzene, which accordingly may be represented by either Baeyer's or Kekulé's formula.[1]

Bamberger, however, in extending Baeyer's views to other compounds, has shown that a great number of facts are much more readily explained by means of the new formulæ than by the old ones. One example will be sufficient to prove this. The hydrocarbon naphthalene, $C_{10}H_8$, has a great resemblance to benzene, and its constitution may be expressed by the two following formulæ:—





Concentrated nitric acid converts benzene into nitrobenzene, $C_6H_5 . NO_2$, and naphthalene into nitronaphthalene, $C_{10}H_7 . NO_2$. By the action of reducing agents the former is converted into amidobenzene or aniline, $C_6H_5 . NH_2$, and the latter into amidonaph-

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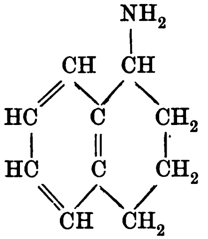
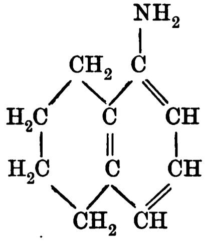
[1] *Ann. Chem. Pharm.* 251, 257.

thalene or naphthylamine, $C_{10}H_7 . NH_2$, which can be combined with four atoms of hydrogen, yielding two different tetrahydronaphthylamines, $C_{10}H_{11} . NH_2$, having, if we adopt the first of the above formulæ, the following constitution :—





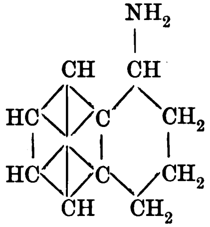
Other derivatives of naphthalene yield similar addition products, which form two distinct groups. The compounds of the first group contain the four additive hydrogen atoms in the substituted nucleus, which in the above case contains the amido group. Bamberger calls these bodies *alicyclic* compounds (*ἄλειφαρ*, fat; and *κύκλος*, ring), because they behave like fatty bodies, but contain the carbon atoms arranged in a closed chain.

The bodies belonging to the second group, containing the four hydrogen atoms in the non-substituted nucleus, are called aromatic compounds, because they exhibit the behaviour of such bodies.

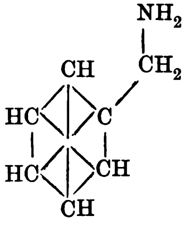
But the most striking fact is that the two tetrahydronaphthalenes exhibit the strongest resemblance to certain derivatives of benzene. Thus, the first or alicyclic compound exhibits almost all the properties of phenylmethylamine, $C_6H_5 . CH_2 . NH_2$; whilst the second or aromatic compound, shows much less analogy with naphthylamine than with aniline, and can hardly be distinguished from amidodimethylbenzene or xylidine, $C_6H_3(CH_3)_2NH_2$.

The above formulæ do not account for these facts, but they can be readily explained by adopting Bamberger's formula for naphthalene, which, as well as his naphthylamine formula, does not contain the aromatic or benzene group. But by the addition of four hydrogen atoms such a group is formed, and consequently the constitution of the tetrahydronaphthalenes is very similar to that of the benzene derivatives mentioned above, as the following formulæ will show[1] :—

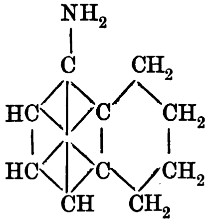
ac-Tetrahydronaphthylamine.



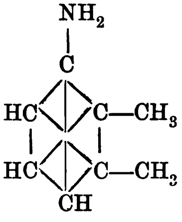
Phenylmethylamine.



ar-Tetrahydronaphthylamine.



Xylidine.



Among the aromatic, as well as among the aliphatic compounds there are found a certain number, behaving in such a way that it is not possible to

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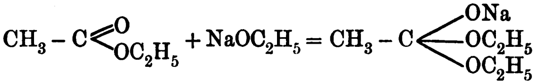
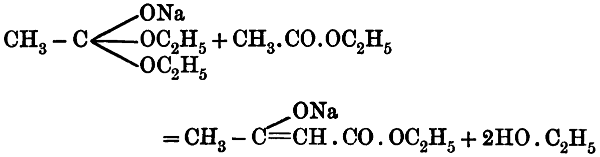
[1] *Ann. Chem. Pharm.* 257, 1, etc.

explain all their reactions by means of one constitutional formula. Such a compound is aceto-acetic ester. In preparing this compound from ethyl acetate it has been found that the latter is only acted upon by sodium if it contains a little alcohol. The reason of this is, according to Claisen, that for the formation of aceto-acetic ester the presence of sodium ethylate is necessary, this forming with ethyl acetate a very unstable intermediate compound—



$$CH_3-C\begin{array}{l}\nearrow\!\!\nearrow O\\ \searrow OC_2H_5\end{array}+NaOC_2H_5=CH_3-C\begin{array}{l}\nearrow ONa\\ -OC_2H_5\\ \searrow OC_2H_5\end{array}$$

This is at once further acted upon by a second molecule of ethyl acetate, the sodium compound of aceto-acetic ester being formed—

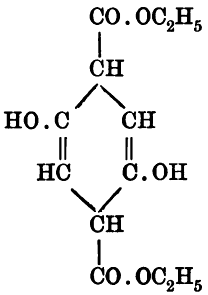


$$CH_3-C\begin{array}{l}\nearrow ONa\\ -OC_2H_5\\ \searrow OC_2H_5\end{array}+CH_3.CO.OC_2H_5$$

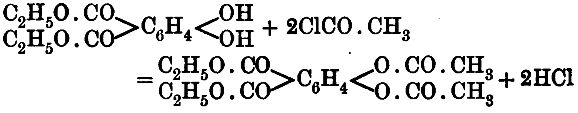
$$=CH_3-\overset{\nearrow ONa}{C}{=}CH.CO.OC_2H_5+2HO.C_2H_5$$

This, however, gives a constitution quite different from that given above (p. 171)—$CH_3.CO.CH_2.CO.OC_2H_5$—generally adopted, because in many cases the compound is decomposed with the elimination of acetyl, $CO.CH_3$. On the other hand, aceto-acetic ester behaves in many reactions like a compound containing the group $CH_3-C(OH)=$.

The constitution of succino-succinic ester, which may be formed from aceto-acetic ester, would in accordance with the second formula be as follows :—

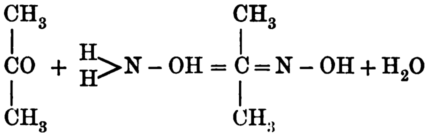


But we come to exactly the same conclusion from the fact that by boiling an alcoholic solution of diethyl dihydroxyterephthalate with hydrochloric acid and zinc, it is converted into succino-succinic ester. This would be diethyl dihydroxydihydroterephthalate, and indeed it behaves as such, for acetyl chloride converts it into a diacetate—



$$\begin{matrix}C_2H_5O.CO\\C_2H_5O.CO\end{matrix}\!>C_6H_4<\!\begin{matrix}OH\\OH\end{matrix} + 2ClCO.CH_3 = \begin{matrix}C_2H_5O.CO\\C_2H_5O.CO\end{matrix}\!>C_6H_4<\!\begin{matrix}O.CO.CH_3\\O.CO.CH_3\end{matrix} + 2HCl$$

On the other hand, if we treat it with hydroxylamine, $N(OH)H_2$, it yields the compound $(C_2H_5O.CO)_2C_6H_6(NOH)_2$, two atoms of oxygen being replaced by the dyad group, $=N-OH$. This reaction is characteristic of the ketones. The most simple of these is acetone, which by hydroxylamine is converted into acetoxime—

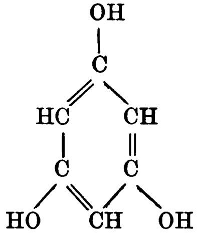


$$\begin{matrix}CH_3\\|\\CO\\|\\CH_3\end{matrix} + \begin{matrix}H\\H\end{matrix}\!>N-OH = \begin{matrix}CH_3\\|\\C\\|\\CH_3\end{matrix}\!=N-OH+H_2O$$

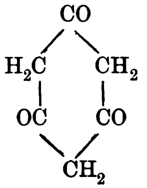
Hence, to explain the action of hydroxylamine upon succino-succinic ester we are obliged to assign to it the formula which we have given before (p. 171), and in which it appears as a ketone.

Baeyer found that phloroglucinol or symmetrical trihydroxybenzene, $C_6H_3(OH)_3$, behaves in the same way. We can easily replace the hydrogen of the hydroxyl by metals, alcohol radicals, and acid radicals; but with hydroxylamine it forms a trioxime, $C_6H_6(NOH)_3$, whence we can express its constitution by two formulæ—

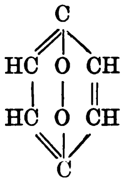
Trihydroxybenzene.

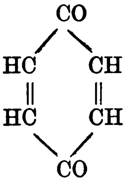


Triketohexhydrobenzene.



We know many similar examples. Quinol or paradihydroxybenzene, $C_6H_4(OH)_2$, is a colourless, odourless crystalline substance, which by oxidation is converted into quinone, $C_6H_4O_2$, forming golden yellow crystals, and having a most pungent smell. In many reactions quinone behaves like a peroxide, in others like a ketone, and its constitution may therefore be represented by the following formulæ:—

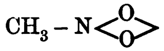




But much more simple compounds must be represented by different constitutional formulæ, such as nitrous acid, NO_2H, and cyanic acid, CNOH, which in the free state are most unstable, but yield stable derivatives of two kinds—

Methyl Nitrite.
$CH_3-O-N=O$

Methyl Cyanate.
$CH_3-O-C\equiv N$

Nitromethane.

$CH_3-N\langle{}^{O}_{O}\rangle$

Methyl Isocyanate.
$CH_3-N=C=O$

It is evident that there exist compounds to which we must assign two different structural formulæ if we want to explain their chemical behaviour. Laar has proposed to call such bodies *tautomeric.*[1]

The atoms within the molecule are in continual motion, and thus one form of a compound changes into another; the light atoms of hydrogen, the comet of the elements, moving the quickest, gets outside the sphere of attraction of a heavier atom, and comes within the sphere of attraction of another atom. But if we replace hydrogen by an element or radical, moving more slowly, the latter does not get beyond the sphere of attraction, and the unstable form becomes a stable one.

Whilst according to the theory of types, one compound could have several rational formulæ, and there was no fixed constitution, the law of the linking of the atoms led to the view, that for each compound only one structural formula was possible. The progress of science has brought us beyond these two

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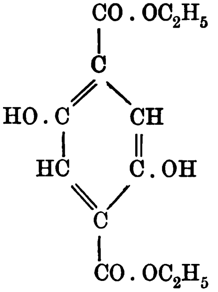
[1] *Ber. deutsch. chem. Ges.* 18, 648; 19, 730.

standpoints by proving the existence of compounds whose behaviour is in opposition to each of the above assumptions in turn. It has forced us to a dialectic treatment of the subject and justified even for molecules the axiom of Heraclitus that everything is in an eternal flux.

P. Jacobson objects to the word Tautomerism because it involves the view that tautomeric bodies do not assume a definite constitution, but are in a continually changing inter-molecular state, whereas he is of opinion, that such compounds exist in both forms and a change of one into the other occurs only by certain reactions. He proposes the term *Desmotropy* (δεσμός, ligament; τρέπειν, to change) because the phenomenon is produced by a change in the linking of the atoms.[1]

Hantzsch and Hermann think we might use both terms, and call desmotropic such tautomeric bodies as exist in two different physical forms,[2] such as ethyl-dihydroxyterephthalate, forming white crystals, having the constitution—



and green crystals in which we have probably the following arrangement:—

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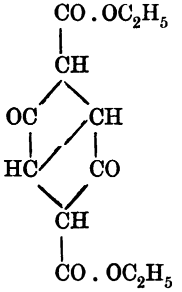
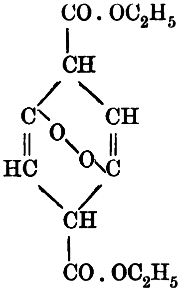
[1] *Ber. deutsch. chem. Ges.* 20, 1732; 21, 2628.

[2] *Ibid.* 20, 2801.

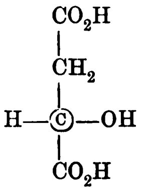


or

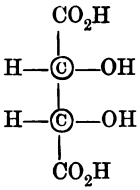


Among the compounds for which an explanation of isomerism was still wanting, Kekulé enumerated those bodies which exist in two different optical modifications, one turning the plane of polarised light to the right and the other to the left. Le Bel and van't Hoff have shown that all such bodies contain one or several *asymmetric* carbon atoms, by which is understood a carbon atom combined with four different kinds of atoms or groups, as the following examples show:—

Malic acid.



Tartaric acid.



We distinguish the two modifications of the latter compound as dextro- and laevotartaric acid; by their combination we obtain the optically inactive racemic acid.

The constitution of such optically opposite bodies may be illustrated by supposing the asymmetric carbon atom to be placed in the centre of a regular tetrahedron, its four bonds being directed towards the corners. By painting the latter with four different colours and doing the same with a second tetrahedron in such a way that it appears as an image in a mirror of the first, we get an idea of the different arrangement of the atoms in space, by which optical isomerism is caused.

If we abstract the elements of one molecule of water from malic acid, we obtain two isomeric compounds called fumaric and maleïc acid, $C_4H_4O_4$; these bodies also formed an example of unexplained isomerism. Kekulé afterwards found that both combined with hydrogen to form succinic acid, $C_4H_6O_4$; whilst by union with bromine two isomeric dibromosuccinic acids, $C_4H_4Br_2O_4$, were formed. From this the conclusion was drawn that fumaric and maleïc acid contained free combining units. The dibromosuccinic acid which is obtained from fumaric acid is also formed by the action of bromine on succinic acid, and by replacing the bromine by hydroxyl, is converted into inactive tartaric acid, differing from racemic acid by not being a combination of the left and right-handed acids.

Kekulé therefore proposed the following formulæ:—

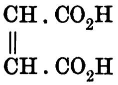
Fumaric. Maleïc.

$$\begin{array}{l} -CH.CO_2H \\ \;\,| \\ -CH.CO_2H \end{array} \qquad \begin{array}{l} =C.CO_2H \\ \;\,| \\ CH_2.CO_2H \end{array}$$

Subsequently, however, he and Swarts came to the conclusion that in fumaric acid the two carbon atoms were joined by a double linking, whilst maleïc acid contained free combining units.

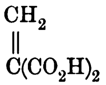
In a similar way Kekulé explained other cases of isomerism; he assumed that those carbon compounds which combine directly with hydrogen, the elements of the chlorine-group, etc., contained either carbon atoms linked together by more than one of their combining units, or that gaps,—that is to say, free combining units, existed in them. The latter view has been abandoned by most chemists. If fumaric and maleïc acids do not contain free combining units, their constitution might be explained by the following formulæ:—

Fumaric acid.



$$\begin{array}{l} CH\,.\,CO_2H \\ \| \\ CH\,.\,CO_2H \end{array}$$

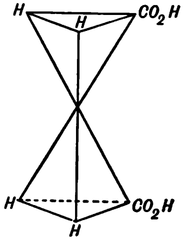
Maleïc acid.



$$\begin{array}{l} CH_2 \\ \| \\ C(CO_2H)_2 \end{array}$$

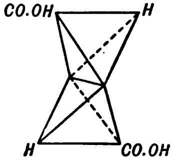
But there are weighty reasons for not accepting this formula for maleïc acid. When heated it loses water and is converted into an anhydride, whilst acids containing two carboxyls combined with one and the same carbon atom are resolved into carbon dioxide and a monobasic acid. Thus isosuccinic acids, $CH_3.CH(CO_2H)_2$, yields propionic acid, $CH_3.CH_2\,.\,CO_2H$, and maleïc acid should, therefore, when heated, be decomposed into carbon dioxide and acrylic acid, $CH_2 = CH\,.\,CO_2H$. Moreover, on combining with hydrogen it could not yield succinic acid, but isosuccinic acid. Besides this, fumaric and maleïc acids may easily be converted one into the other—a fact which is not in consonance with the above formulæ.

Van't Hoff has brought forward another hypothesis, according to which the isomerism of the two acids cannot be explained by our usual graphic formulæ, because they represent the position of the atoms in a plane instead of in space of three dimensions. If we imagine again the four combining units of a carbon atom to be directed towards the corners of a tetrahedron, in the centre of which the atom is placed, we obtain for succinic acid the following glyptic formula:—

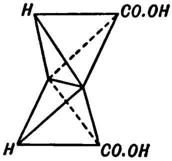


In this case no isomeric compound can exist, because if we arrange the carboxyls or hydrogen atoms of each tetrahedron in any other way, we can by rotating one or the other tetrahedron always obtain the above figure. But by abstracting two atoms of hydrogen, two isomeric acids can be formed[1]—

Fumaric acid.

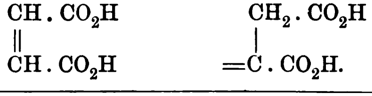


Maleïc acid.



In maleïc acid the carboxyls must be close together to admit of the formation of an anhydride.

Fittig, who in conjunction with his pupils examined these acids most carefully, came to the conclusion that maleïc acid contained free combining units, and that the acids had the following constitution:—



$$\begin{array}{l} CH.CO_2H \\ \| \\ CH.CO_2H \end{array} \qquad \begin{array}{l} CH_2.CO_2H \\ \ \ | \\ =C.CO_2H. \end{array}$$

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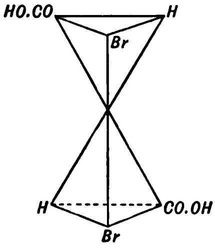
[1] *La chimie dans l'espace; die Lagerung der Atome im Raum. deutsch bearbeitet von Herrmann.*

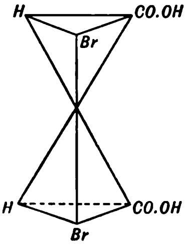
These formulæ were meant to explain why maleïc acid combines more readily than fumaric acid with bromine; they account further for the fact that the acids can be readily transformed one into the other, and that by electrolysis both yield acetylene, CH : CH.

But Kekulé and Anschütz have since found that on oxidation with potassium permanganate, fumaric acid is transformed into racemic acid, and maleïc acid into inactive tartaric acid; and Demuth and Meyer have shown that isodibromosuccinic acid obtained from maleïc acid is easily converted into racemic acid. Fittig's hypothesis can therefore no longer be maintained.

Van't Hoff's hypothesis has been further developed by Wislicenus, who employs the term *geometrical isomerism* for isomerism produced by a different grouping of the atoms in space, a term which has since been changed into the more appropriate one: *stereo-chemical isomerism.*

Maleïc and fumaric acid combine directly with bromine, yielding two isomeric dibromosuccinic acids, to which, according to Wislicenus, the following constitution must be assigned[1]:—





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[1] *Über die räumliche Anordnung der Atome in organischen Molecülen,* 1887.

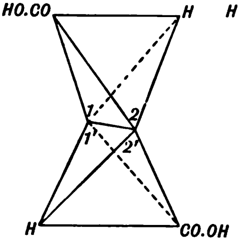
In this case we may turn the tetrahedrons however we like, the two figures will never become identical.

These two dibromo acids correspond to two of the four modifications of tartaric acid. Of these only the right-handed form (dextrotartaric acid) is found in grapes and other kinds of fruit, whilst racemic acid which was supposed to occur also in nature, is produced during the manufacture of dextrotartaric acid, and may be completely converted into it by heating with a little water to 175°.

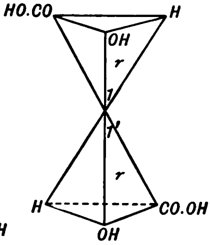
On the other hand Pasteur showed long ago that racemic acid could be resolved into the two optically opposite modifications by converting it into the sodium-ammonium double salt. In this way two kinds of crystals are obtained, one of them showing small hemihedral faces on one side, and the other on the opposite side, so that the latter kind appears like the image of the former in a mirror. If we separate these crystals and again isolate the acids, we obtain from one kind the right-handed and from the other the left-handed modification. On mixing equal quantities of the concentrated solutions of the two acids, heat is evolved, and on cooling, racemic acid crystallises out. It is a combination of the two active acids, and is less soluble in water.

When we act on fumaric acid with a solution of potassium permanganate it is converted into racemic acid, a direct addition of hydroxyl, OH, taking place. If in Fig. I. the double linking is loosened at 1, 1′ we find that in both tetrahedrons of Fig. II. the sequence of CO_2H, OH, H is in the opposite direction to that in the tetrahedrons of Fig. III., which is formed by the hydroxyls combining at the points 2, 2′; and further on comparing the lower tetrahedrons with the upper they will be found superposable, whilst Fig. II. bears to Fig. III. the same relation as an object to its image in a mirror—

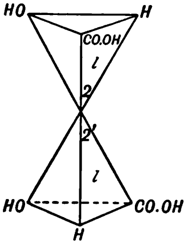
I



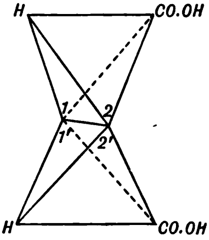
II

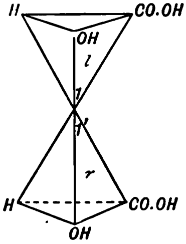


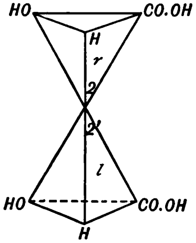
III



Maleïc acid combines with hydroxyl to form inactive tartaric acid, in which half the molecule is right-handed and the other left-handed, and thus the lower tetrahedrons in the following figures are not superposable in respect to the upper tetrahedra:—

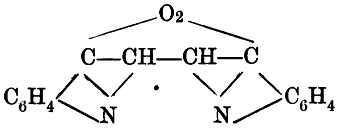


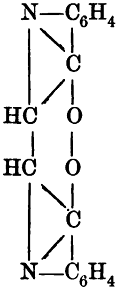




Inactive tartaric acid cannot be resolved into the two active acids like racemic acid, but it is changed into the latter if we heat it with some water to 175°.

Kolbe never recognised the law of the linking of atoms, and he attacked the modern "Structurchemiker" most vehemently. He called Kekulé a chemical poet, whose views on the constitution of chemical compounds were phantasmagoria. The crude endeavour to illustrate the supposed position of atoms in space by means of mechanical drawings was nothing but a vain juggling with formulæ. Baeyer, in his brilliant researches on indigo, which will be mentioned hereafter, had proposed the following formula for this body :—





Kolbe says of the first: "This is indigo *à la* umbrella, the roof and the knob are there, but it wants —*a stick!*" The second picture shows us indigo *à la* tower-steps.

The motion of atoms in space, their rebounding from each other within the molecule, their sticking together, the hooks by which they catch each other, were hallucinations.

Of van't Hoff's book he says: "A certain Dr. J. H. van't Hoff, an official of the Veterinary School at Utrecht, has, it seems, no taste for exact chemical investigation. He has thought it more convenient to bestride Pegasus (evidently hired at the veterinary stables), and to proclaim in his *La chimie dans l'espace*, how during his bold flight to the top of the chemical

Parnassus, the atoms appeared to him to have grouped themselves throughout universal space."

As a warning for those who are exposed to the danger of losing their understanding of exact chemistry by the phrases of the modern doctrines, he gives the following somewhat modified quotation from *Faust* :—

> Nachher vor allen anderen Sachen
> Müsst' Ihr Euch an die 'Structurchemie' machen,
> Da seht, dass Ihr *tiefsinnig* fasst,
> *Was in des Menschen Hirn nicht passt* ;
> Für was drein geht und nicht drein geht,
> Ein prächtig Wort zu Diensten steht.

Kolbe speaks repeatedly of Berzelius as his master and guide. By strictly adhering to the exact scientific principles prescribed by Berzelius, he had harvested bountiful fruit. The modern chemists were influenced by preconceived opinions and they established dogmas founded on philosophical abstractions. His endeavour was to destroy such chemical ill-weeds.

Kolbe could not be brought to see that for the development of all branches of natural science we continually require new hypotheses. That we find among them some that are futile cannot be helped; we can, however, soon deal them their deserts.

But the stern logic of facts obliged Kolbe to change his views continually. He first opposed the new atomic weights of carbon and oxygen which Gerhardt introduced; but after he had accepted them, he pointed out that he had been the first to recognise the tetravalency of carbon, by showing that it occurred in most of its compounds as "a tetrad double atom." He had not made use of the term tetrad, as this feature was self-evident.

Benzene was regarded by him as triacetylene, having the following formula:—

$$\left.\begin{matrix}\mathrm{CH}\\ \mathrm{CH}\end{matrix}\right\}\mathrm{CH,CH}\left\{\begin{matrix}\mathrm{CH}\\ \mathrm{CH}\end{matrix}\right.$$

By means of this formula he explained the isomerism of the disubstitution products exactly as Kekulé. In place of lines he used the comma and brackets. As Kekulé pointed out, this formula coincides with Ladenburg's; but Kolbe maintained that they were essentially different. "My formula is the definite expression of a chemical idea, and, before I constructed it, the idea was carefully developed. According to it, benzene is in the first place derived from methane, and stands in the most proximate relation to diethylene, which has not yet been isolated, but which undoubtedly can be obtained."

The structural formulæ for benzene did not contain this idea; they were only schemes from which we might perceive how the atoms of carbon and hydrogen were combined, without an affinity remaining unsaturated.

Kolbe was of opinion that the chemists of the day were nothing but "Naturphilosophen."

X

The synthesis of organic compounds—Urea—Acetic acid—Paraffins—Alcohols and fatty acids—Glycerol and fats—Vegetable acids—Sugar—Conine—Uric acid.

WÖHLER'S important discovery that ammonium cyanate changes easily into urea could not be regarded as the synthesis of an organic compound, because, as already stated, at that time no method was known for obtaining cyanogen compounds directly from their elements. Until 1845 no other organic body was prepared from its elements, but in that year Kolbe discovered a simple synthesis of acetic acid. On heating sulphur with charcoal, we obtain carbon disulphide, CS_2, which by the action of chlorine is converted into tetrachloromethane, CCl_4, and this when passed as vapour through a red-hot tube yields free chlorine and tetrachlorethylene, C_2Cl_4. The latter combines again with chlorine to form hexachlorethane, and if the action takes place in direct sunlight and in the presence of water, a part of the tetrachlorethylene is converted into trichloracetic acid—

$$CCl_2 : CCl_2 + Cl_2 + 2H_2O = CCl_3 . CO . OH + 3HCl$$

Kolbe then replaced the chlorine by hydrogen, by Melsen's method (p. 47), and found that this may also be effected by passing a galvanic current through an aqueous solution of trichloracetic acid, using as electrodes two amalgamated zinc-plates.[1]

Regnault found subsequently that by the action of potassium amalgam on an alcoholic solution of tetrachloromethane, the latter was again converted into marsh-gas from which it had been obtained by substitution.[2] Thus it was proved that this hydrocarbon could be obtained synthetically by two methods, either by starting with carbon disulphide, or by heating acetic acid with an alkali. Another synthesis, which Berthelot discovered, has already been mentioned (p. 89).

Before 1848 marsh gas was the only member of the paraffins which was at all well known. But at that time the researches of Kolbe on the electrolysis of the fatty acids, and those of Frankland on the action of zinc upon the iodides of the alcohol radicals, opened a new field of discovery from which a rich harvest was soon reaped. As already mentioned the hydrocarbons thus obtained were first regarded as free alcohol radicals. In their report to the French Academy, Laurent and Gerhardt proposed that the formula of these hydrocarbons should be doubled in accordance with Avogadro's law. They regarded them as true homologues of marsh gas, and this view was also taken by Hofmann, who pointed out that if the formulæ of Kolbe and Frankland were accepted, the increment of the boiling-point produced by each addition of CH_2 would be twice what it ought to be according to Kopp's law.

Besides the so-called radicals, Frankland discovered another series of hydrocarbons which, in accordance

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[1] *Ann. Chem. Pharm.* 54, 181.

[2] *Cours élémentaire de chimie,* 4, 274 ; Gerhardt, *Traité,* 1, 603.

with the mode of formation, he regarded as the hydrides of the alcohol radicals, and as true homologues of marsh gas, standing to the radicals, as Brodie pointed out, in the same relation as the alcohols to the ethers—

Ethyl hydride	$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}$	Ethyl alcohol	$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$
Ethyl	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}$	Ethyl ether	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$

Brodie also anticipated the existence of mixed radicals, bearing to the simple radicals the same relation as Williamson's mixed ethers bore to the simple ethers—

Ethylamyl	$\left.\begin{matrix}C_2H_5\\C_5H_{11}\end{matrix}\right\}$	Ethylamyl ether	$\left.\begin{matrix}C_2H_5\\C_5H_{11}\end{matrix}\right\}O$

These mixed radicals were discovered by Wurtz, who obtained them by the action of sodium on a mixture of two iodides such as those of ethyl and amyl. These results were considered as a convincing proof of the correctness of the view that the homologues of marsh gas formed two distinct groups (1) the hydrides and (2) the coalesced radicals, two radicals combining to form a molecule, just as two atoms of hydrogen unite to form one.

It was not until 1865 that the author found that no difference existed between the two classes. By the action of chlorine on ethylamyl he obtained a heptyl chloride, $C_7H_{15}Cl$; whilst both dimethyl and ethyl hydride yielded ethyl chloride. The identity of the supposed two groups was thereby established.

Thus the views of Laurent and Gerhardt received striking confirmation, and proof was afforded that the methods of Frankland and Wurtz were real syntheses.

Other methods for the synthesis of paraffins will be described later. By the action of chlorine the paraffins yield, as first substitution products, monochlorides; from these the alcohols and their derivatives, such as the fatty acids, may be obtained, though they are more readily prepared by other synthetical methods.

Kolbe and Frankland, as well as Dumas, Malaguti, and Leblanc, had found, in 1847, that by boiling the cyanides of the alcohol radicals with caustic potash, they were converted into fatty acids containing one carbon atom more than the alcohols from which the cyanides were obtained. This reaction afterwards became of the highest importance in the synthesis of organic bodies.

A similar synthesis, however, had been observed by Winkler in 1832; by the action of prussic acid and hydrochloric acid on oil of bitter almonds or benzaldehyde, C_7H_6O, he obtained mandelic or phenylglycollic acid, $C_8H_8O_3$, which four years later was carefully examined by Liebig. By the same reaction Strecker converted common aldehyde into lactic acid (p. 126), but it was not till long afterwards that these reactions were recognised as syntheses.

These examples show that by organic synthesis we understand not only the building up of compounds from the elements, but also the linking of carbon atoms. To the latter class of syntheses belongs also the artificial preparation of oil of cinnamon, which Chiozza effected in 1856, by heating oil of bitter almonds with aldehyde and hydrochloric acid—

$$C_6H_5.CHO + CH_3.CHO = C_6H_5.CH : CH.CHO + H_2O$$

Oil of cinnamon is the aldehyde of cinnamic acid which Bertagnini obtained in the same year by heating oil of bitter almonds with acetylchloride—

$$C_6H_5 . CHO + CH_3 . COCl = C_6H_5 . CH : CH . COCl + H_2O$$
$$= C_6H_5 . CH : CH . CO . OH + HCl$$

Another important synthesis was discovered in 1858 by Wanklyn, who found that sodium ethide combines with carbon dioxide to form sodium propionate—

$$C_2H_5Na + CO_2 = C_2H_5 . CO_2Na$$

In the next year Berthelot solved a problem which had occupied chemists for a long time, viz. the direct combination of carbon and hydrogen. He effected this by producing the electric arc between two carbon poles in an atmosphere of hydrogen, acetylene, C_2H_2, being produced. This can unite with more hydrogen to form ethylene, C_2H_4, and ethane, C_2H_6.

After this the synthesis of organic compounds made rapid progress. A favourite problem for chemists had always been to reduce the fatty acids, which occur in nature, to the alcohols and so complete the series of the latter, which contained many gaps. If this could be done, we might go further and build up the whole series of fatty acids as well, since the latter are easily obtained from the alcohols by the reaction previously described. A solution appeared to be found, when Mendius made the discovery that the cyanides combined with nascent hydrogen and yielded amines, methyl cyanide or acetonitrile being thus converted into ethylamine—

$$CH_3 . CN + 4H = CH_3 . CH_2 . NH_2$$

Hofmann had previously found that nitrous acid transforms the amines into alcohols—

$$CH_3 . CH_2 . NH_2 + NO . OH = CH_3 . CH_2 . OH + N_2 + H_2O$$

From ethyl cyanide we ought similarly to obtain propyl alcohol, $C_3H_7 . OH$. This is indeed formed, but at the same time some propylene, C_3H_6, is produced which partially combines with water to form secondary propyl alcohol, and so the simplicity of the reaction comes to an end.

The problem has been solved in another way. In 1852 Williamson pointed out that on heating the calcium salt of a fatty acid with calcium formate it ought to be reduced to its aldehyde[1]—

$$(CH_3 . CO . O)_2Ca + (H . CO . O)_2Ca = 2CH_3 . CHO + 2CaCO_3$$

This reaction, corresponding to the formation of ketones from two molecules of fatty acids (p. 144), was realised by Piria[2] and Limpricht.[3] Wurtz then found that the aldehydes unite with nascent hydrogen to form alcohols,[4] and thus the way was opened for a systematic building up of the alcohols and fatty acids. But several difficulties had still to be overcome, and it was only in 1869 that Lieben and Rossi succeeded in perfecting the method to such an extent that, starting with common alcohol, we can build up the whole series of the primary alcohols and the fatty acids.

We first convert alcohol into ethyl cyanide or the nitrile of propionic acid; from this we obtain the acid, and heat its calcium salt with calcium formate. We thus get propionaldehyde which we combine with hydrogen to form propyl alcohol, and from this we

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[1] *Ann. Chem. Pharm.* 81, 87.

[2] *Ibid.* 100, 104.

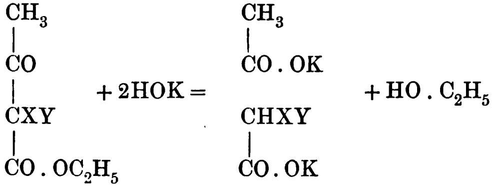
[3] *Ibid.* 101, 291.

[4] *Compt. rend.* 54, 914.

obtain successively butyronitrile, butyric acid, butyraldehyde, and butyl alcohol. Lieben and Rossi extended this reaction up to octyl alcohol, $C_8H_{18}O$, whilst Krafft subsequently prepared some higher homologues, the last being octadecyl alcohol, $C_{18}H_{38}O$. This alcohol corresponds to stearic acid, and is found together with cetyl or hexadecyl alcohol, $C_{16}H_{34}O$, in spermaceti. The highest member, so far known, is myricyl alcohol, $C_{30}H_{62}O$ which is found in beeswax.

Another method, discovered by Frankland and Duppa and perfected by other chemists, enables us to synthesise not only the fatty acids but also a great number of compounds of different homologous series. The principle of this method is to replace hydrogen in the methyl of acetic acid by carbon radicals. We first convert the acetic acid into aceto-acetic ester, $CH_3 . CO . CH_2 . CO_2 . C_2H_5$, and convert this by means of sodium or sodium ethylate into pure sodaceto-acetic ester, $CH_3 . CO . CHNa . CO_2 . C_2H_5$ (p. 171). If we act upon this with an alcohol iodide, such as methyl iodide, the sodium is replaced by the alcohol radical. In the methylaceto-acetic ester thus obtained we can again replace one atom of hydrogen by sodium, $CH_3 . CO . C(CH_3)Na . CO_2 . C_2H_5$, and this in turn by an alcohol radical.

All these compounds are decomposed by strong potash like aceto-acetic ester itself, according to the following equation :—



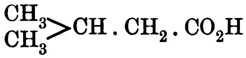
$$\begin{array}{l}CH_3\\ |\\ CO\\ |\\ CXY\\ |\\ CO . OC_2H_5\end{array} + 2HOK = \begin{array}{l}CH_3\\ |\\ CO . OK\\ \\ CHXY\\ |\\ CO . OK\end{array} + HO . C_2H_5$$

In these formulæ X and Y stand for hydrogen or any alcohol radical. It is evident that by means of this reaction we can obtain not only homologous but also isomeric acids—

Pentoic or Propylacetic acid.

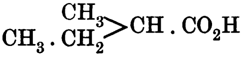
$$CH_3 . CH_2 . CH_2 . CH_2 . CO_2H$$

Valerianic or Isopropylacetic acid.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH . CH_2 . CO_2H$$

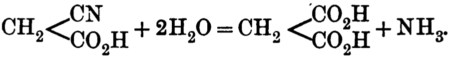
Methylethylacetic acid.



$$\begin{matrix}CH_3\\CH_3 . CH_2\end{matrix}\!\!>CH . CO_2H$$

The first of these is obtained by replacing one atom of hydrogen in acetic acid by primary propyl, whilst by introducing secondary propyl we get valerianic acid. To prepare the third acid, we act on the sodium compound with ethyl iodide, treat the ethyl-aceto-acetic ester, $CH_3 . CO . C(C_2H_5)H . CO_2C_2H_5$, with sodium, and convert the sodium compound by means of methyl iodide into ethylmethylaceto-acetic ester, which we decompose by potash.

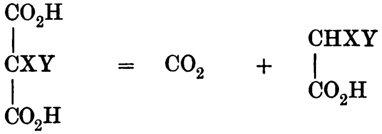
The higher fatty acids can also be obtained from acetic acid by another reaction, by which the latter is first converted into chloracetic acid, $CH_2Cl . CO_2H$. In this we replace the chlorine by cyanogen, and heat the cyanacetic acid with potash, which converts it into dibasic malonic acid—



$$CH_2\!<\!\begin{matrix}CN\\CO_2H\end{matrix} + 2H_2O = CH_2\!<\!\begin{matrix}CO_2H\\CO_2H\end{matrix} + NH_3.$$

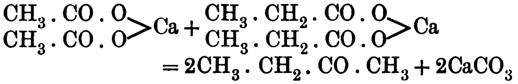
Conrad has shown that in diethyl malonate, $CH_2(CO_2 .$

$C_2H_5)_2$, we can replace the hydrogen successively by sodium and alcohol radicals. From the compounds thus obtained, we can easily prepare the free acids, which are resolved by heat into carbon dioxide and a fatty acid—



$$\begin{array}{c} CO_2H \\ | \\ CXY \\ | \\ CO_2H \end{array} = CO_2 + \begin{array}{c} CHXY \\ | \\ CO_2H \end{array}$$

The formation of ketones, which, as Williamson has shown, are obtained by the dry distillation of the calcium salts of the fatty acids, also affords a mode of synthesis. Acetic acid yields acetone or dimethyl ketone, whilst if we use a mixture of the calcium salts of acetic and propionic acid, we obtain methylethyl ketone—



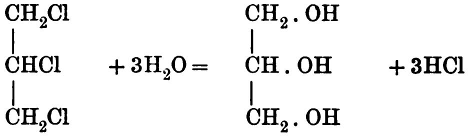
$$\left.\begin{array}{l} CH_3 . CO . O \\ CH_3 . CO . O \end{array}\right> Ca + \left.\begin{array}{l} CH_3 . CH_2 . CO . O \\ CH_3 . CH_2 . CO . O \end{array}\right> Ca$$
$$= 2CH_3 . CH_2 . CO . CH_3 + 2CaCO_3$$

On heating a ketone with hydriodic acid and amorphous phosphorus the oxygen is replaced by hydrogen and a paraffin is formed. By this reaction Krafft completed the series of the normal compounds up to pentatriacontane, $C_{35}H_{72}$ (p. 142). By means of the ketones we can also go downwards in the series of the fatty acids. The higher acids occurring in nature all contain an even number of carbon atoms. In his classical researches on the fats, Chevreul believed that in the different kinds of tallow there existed besides palmitic acid, $C_{16}H_{32}O_2$, and stearic acid, $C_{18}H_{36}O_2$, the intermediate margaric acid, $C_{17}H_{34}O_2$. This was afterwards found to be a mixture of the two others, and margaric acid is not found in nature. We can, however, obtain margaric acid by synthesis according to the method described, or, more simply, by reducing palmitic acid to hexadecylaldehyde, converting this into the alcohol and the latter into the cyanide, which when heated with caustic potash yields margaric acid. But it is obtained much more simply by distilling a mixture of calcium acetate and stearate, by which we obtain methyl heptadecyl ketone, $C_{17}H_{35}.CO.CH_3$. This by oxidation is resolved into acetic acid and margaric acid.

By the researches of Chevreul and Berthelot it was shown that fats belong to the class of ethereal salts or esters; on heating them with an alkali we obtain soap, consisting of a mixture of salts of the fatty acids, and glycerin or glycerol, $C_3H_5(OH)_3$. Berthelot further showed that on heating the latter compound with a fatty acid we obtain again a simple fat, butyric acid yielding propenyltributyrate or tributyrin—

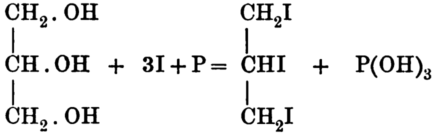
$$C_3H_5(OH)_3 + 3HO.CO.C_3H_7 = C_3H_5(O.CO.C_3H_7)_3 + 3H_2O$$

For a synthesis of fats it was now only necessary to find a method for building up glycerol or propenyl alcohol from its elements, and this Friedel and de Silva succeeded in doing. They started with acetone, which can be obtained synthetically from acetic acid and by other methods (p. 144), and which by the action of nascent hydrogen is converted into secondary propyl alcohol, $CH_3.CH(OH).CH_3$. From this they obtained propylene, $CH_3.CH:CH_2$, and by heating its dichloride, $CH_3.CHCl.CH_2Cl$, with iodine chloride they got propenyl trichloride, $CH_2Cl.CHCl.CH_2Cl$. When this is heated with water under pressure, glycerol is formed—



$$\begin{array}{l} CH_2Cl \\ | \\ CHCl \\ | \\ CH_2Cl \end{array} + 3H_2O = \begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} + 3HCl$$

Berthelot and de Luca found in 1854 that by acting on glycerol with iodine and phosphorus, it is converted into allyl iodide, the first product being propenyl tri-iodide—



$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} + 3I + P = \begin{array}{l} CH_2I \\ | \\ CHI \\ | \\ CH_2I \end{array} + P(OH)_3$$

The tri-iodide is then resolved into free iodine and allyl iodide, $CH_2:CH.CH_2I$. On heating this with potassium sulphide we obtain allyl sulphide, $(C_3H_5)_2S$, which forms the chief constituent of the essential oil of garlic, onions, etc., and appears also to be present in asafœtida. Allyl thiocarbimide, C_3H_5NCS, or mustard oil is easily obtained by heating the iodide with potassium thiocyanate.

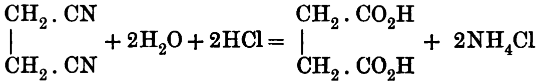
Hofmann afterwards prepared a number of other thiocarbimides or "mustard oils," which resemble common oil of mustard. Of these the secondary butyl thiocarbimide, $C_2H_5.CH(NCS)CH_3$, forms the chief constituent of the essential oil of scurvy grass.

The following acids which are nearly related to each other, are frequently met with in plants:—

Succinic Acid	$C_4H_6O_4$
Malic Acid	$C_4H_6O_5$
Tartaric Acid	$C_4H_6O_6$

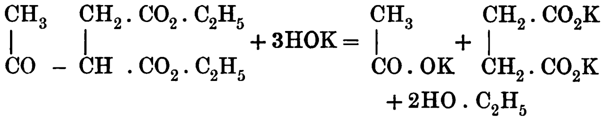
Maxwell Simpson has shown that succinic acid can be obtained synthetically by heating ethylene dibromide,

$C_2H_4Br_2$, with potassium cyanide, and then acting on the ethylene dicyanide or succinonitrile with hydrochloric acid—



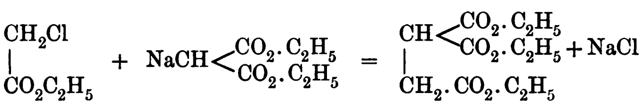
$$\begin{array}{l}CH_2.CN\\ |\\ CH_2.CN\end{array} + 2H_2O + 2HCl = \begin{array}{l}CH_2.CO_2H\\ |\\ CH_2.CO_2H\end{array} + 2NH_4Cl$$

Succinic acid has also been prepared by acting on sodaceto-acetic ester with ethyl chloracetate to form diethyl-acetosuccinate, and boiling the product with potash—



$$\begin{array}{lcl}CH_3 & & CH_2.CO_2.C_2H_5\\ | & & |\\ CO & - & CH\ .CO_2.C_2H_5\end{array} + 3HOK = \begin{array}{l}CH_3\\ |\\ CO.OK\end{array} + \begin{array}{l}CH_2.CO_2K\\ |\\ CH_2.CO_2K\end{array} + 2HO.C_2H_5$$

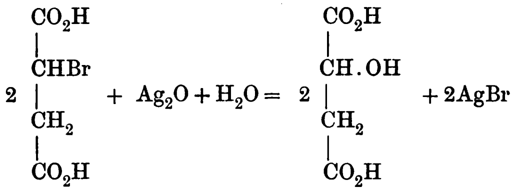
By treating the sodium compound of diethyl malonate with ethyl chloracetate we get the ethyl ester of ethenyltricarboxylic acid—



$$\begin{array}{l}CH_2Cl\\ |\\ CO_2C_2H_5\end{array} + NaCH{<}\begin{array}{l}CO_2.C_2H_5\\ CO_2.C_2H_5\end{array} = \begin{array}{l}CH{<}\begin{array}{l}CO_2.C_2H_5\\ CO_2.C_2H_5\end{array}\\ |\\ CH_2.CO_2.C_2H_5\end{array} + NaCl$$

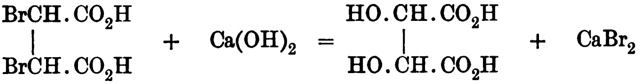
From this we obtain the acid, which on heating is resolved into carbon dioxide and succinic acid.

On heating succinic acid with bromine we obtain monobromsuccinic acid, which, as Kekulé has found, is converted into malic acid by heating it with water and silver oxide—



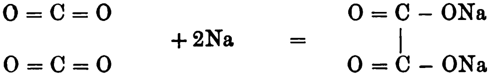
$$2\begin{array}{l}CO_2H\\ |\\ CHBr\\ |\\ CH_2\\ |\\ CO_2H\end{array} + Ag_2O + H_2O = 2\begin{array}{l}CO_2H\\ |\\ CH.OH\\ |\\ CH_2\\ |\\ CO_2H\end{array} + 2AgBr$$

By the further action of bromine on succinic acid we obtain dibromosuccinic acid which, as Kekulé as well as Perkin and Duppa found, is converted into tartaric acid by boiling it with milk of lime or by boiling its silver salt with water—



$$\begin{array}{l} BrCH.CO_2H \\ | \\ BrCH.CO_2H \end{array} + Ca(OH)_2 = \begin{array}{l} HO.CH.CO_2H \\ | \\ HO.CH.CO_2H \end{array} + CaBr_2$$

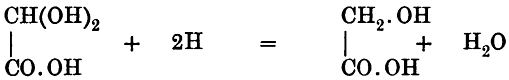
Another interesting synthesis of tartaric acid was discovered by Debus, who obtained it from oxalic acid. This, as Kolbe found, is obtained synthetically by passing carbon dioxide over sodium at 350°—



$$\begin{array}{l} O=C=O \\ \\ O=C=O \end{array} + 2Na = \begin{array}{l} O=C-ONa \\ \quad | \\ O=C-ONa \end{array}$$

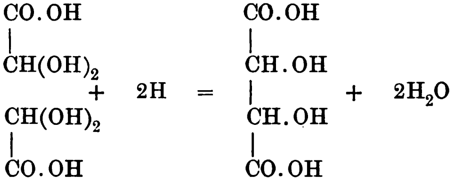
Nascent hydrogen converts oxalic acid into glyoxylic acid and the latter into glycollic acid—

$$\begin{array}{l} CO.OH \\ | \\ CO.OH \end{array} + 2H = \begin{array}{l} CH(OH)_2 \\ | \\ CO.OH \end{array}$$



$$\begin{array}{l} CH(OH)_2 \\ | \\ CO.OH \end{array} + 2H = \begin{array}{l} CH_2.OH \\ | \\ CO.OH \end{array} + H_2O$$

But if we act on an alcoholic solution of ethyl oxalate with sodium-amalgam we obtain, besides these two acids, tartaric acid, the nascent hydrogen acting on two molecules of glyoxylic acid—



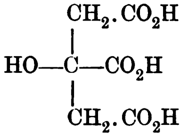
$$\begin{array}{l} CO.OH \\ | \\ CH(OH)_2 \\ \\ CH(OH)_2 \\ | \\ CO.OH \end{array} + 2H = \begin{array}{l} CO.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CO.OH \end{array} + 2H_2O$$

Thus a few simple steps lead us from carbon dioxide, one of the principal foods of plants, to an important vegetable acid, and still more interest is imparted to this synthesis by the fact that glycollic acid is found in the green leaves of the Virginian creeper (*Ampelopsis hederacea*), and in unripe grapes, whilst ripe grapes only contain tartaric acid.

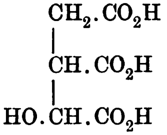
As has been already stated, the artificial tartaric acid is optically inactive, but Jungfleisch found that it is converted into racemic acid by heating it with a little water to 175°, and he succeeded thus in obtaining all four modifications (p. 190) synthetically from ethylene.

Whilst many organic compounds found in nature are optically active, those obtained artificially are inactive, but they can in many cases like that of tartaric acid be converted in active modifications. One of the most simple cases is propylene glycol, $CH_3.CH(OH)CH_2.OH$, which contains an asymmetric carbon atom, but has no action on polarised light. Le Bel has found that on adding to its aqueous solution, *Bacterium termo* and the food of this organism, such as ammonium salts, phosphates and sulphates, fermentation sets in, a portion of the glycol being converted into lactic acid and propionic acid, whilst the remaining portion is now laevo-rotatory. From this we can obtain dextro-rotatory propylene oxide, C_3H_6O, which boils at 35°, and is the most volatile of all known optically active substances.

Citric acid, $C_6H_8O_7$, is frequently found together with malic and tartaric acids. It has also been obtained by synthesis, and serves admirably to show that any organic body can be obtained artificially as soon as its constitution has been ascertained. The first step towards the synthesis was taken by Liebig, who established the true molecular formula of citric acid and showed that the acid was tribasic. On heating it loses one molecule of water and changes into the tribasic aconitic acid, $C_6H_6O_6$, showing that it contains, besides three carboxyls, one hydroxyl, as is further proved by the fact that one of its hydrogen atoms can be replaced by acid radicals. These observations lead to the formula $C_3H_4(OH)(CO_2H)_3$. Aconitic acid combines with hydrogen to form tricarballylic or propenyltricarboxylic acid, which has been obtained from glycerol by replacing its hydroxyls by cyanogen and then converting the latter into carboxyl. Citric acid is therefore hydroxypropenyl tricarboxylic acid, which can exist in two modifications—



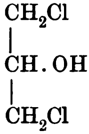
$$\begin{array}{l} \qquad\;\; CH_2.CO_2H \\ \qquad\;\;\; | \\ HO—C—CO_2H \\ \qquad\;\;\; | \\ \qquad\;\; CH_2.CO_2H \end{array}$$



$$\begin{array}{l} \qquad\quad CH_2.CO_2H \\ \qquad\quad | \\ \qquad\quad CH.CO_2H \\ \qquad\quad | \\ HO.CH.CO_2H \end{array}$$

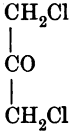
Of these the first appears the more probable, because among the products of decomposition of citric acid we find acetone or its derivatives. The correctness of this view has been proved by Grimaux and Adam, who obtained citric acid from glycerol. By the action of hydrochloric acid glycerol is converted into propenyl dichlorhydrin. This on oxidation gives symmetrical dichloracetone, which combines with hydrocyanic acid to form the nitrile of dichlorhydroxy isobutyric acid. From this the acid was prepared, its sodium salt heated with potassium cyanide to convert it into dicyanohydroxyisobutyric acid, and this by the action of hydrochloric acid was converted into citric acid —

Propenyl Dichlorhydrin.



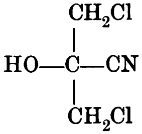
$$\begin{array}{l} CH_2Cl \\ | \\ CH.OH \\ | \\ CH_2Cl \end{array}$$

Dichloracetone.



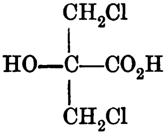
$$\begin{array}{l} CH_2Cl \\ | \\ CO \\ | \\ CH_2Cl \end{array}$$

Dichlorhydroxy-isobutyronitril.



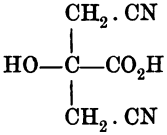
$$\begin{array}{c} CH_2Cl \\ | \\ HO—C—CN \\ | \\ CH_2Cl \end{array}$$

Dichlorhydroxy-isobutyric acid.



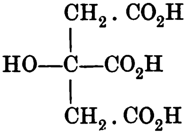
$$\begin{array}{c} CH_2Cl \\ | \\ HO—C—CO_2H \\ | \\ CH_2Cl \end{array}$$

Dicyanohydroxy-isobutyric acid.



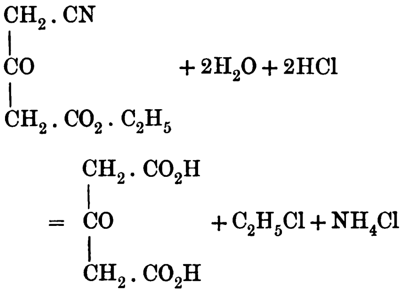
$$\begin{array}{c} CH_2.CN \\ | \\ HO—C—CO_2H \\ | \\ CH_2.CN \end{array}$$

Citric acid.



$$\begin{array}{c} CH_2.CO_2H \\ | \\ HO—C—CO_2H \\ | \\ CH_2.CO_2H \end{array}$$

Two other French chemists, Haller and Held, obtained citric acid from aceto-acetic ester, which by the action of chlorine in the cold yields ethyl chloraceto-acetate, $CH_2Cl.CO.CH_2.CO_2.C_2H_5$. By acting on this with potassium cyanide and treating the product with hydrochloric acid, they obtained acetone dicarboxylic acid—



$$\begin{array}{l} CH_2.CN \\ | \\ CO \qquad\qquad + 2H_2O + 2HCl \\ | \\ CH_2.CO_2.C_2H_5 \end{array}$$

$$= \begin{array}{l} CH_2.CO_2H \\ | \\ CO \qquad\qquad + C_2H_5Cl + NH_4Cl \\ | \\ CH_2.CO_2H \end{array}$$

On combining this with hydrocyanic acid and treating the product $CN.C(OH)(CH_2.CO_2H)_2$ again with hydrochloric acid, it was converted into citric acid.

That the vegetable acids might be built up from carbon dioxide was anticipated by Liebig, as the following passages from his *Letters on Chemistry* will show:—

"The carbon of all parts and constituents of vegetables, and through vegetables, of animals, is derived from *carbonic acid;* all the hydrogen of non-nitrogenised organic bodies (sugar, starch, woody fibre, gums, oils, etc.) is derived from *water.*

"No part of a vegetable or animal organism contains, for one atom of carbon, more than two atoms of another element. The great majority of organic bodies contain, for one atom of carbon, less than two other atoms.

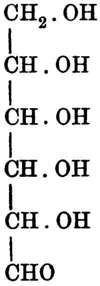
"All the constituents of organisms are formed of atoms of carbonic acid, more or less modified, or of groups of such atoms, having been produced, under the influence of solar light, from the carbonic acid absorbed by the roots and leaves of plants. The change is the result of separation and extrusion of part of the oxygen of the carbonic acid atoms, in the place of which oxygen there is taken up hydrogen, or hydrogen and nitrogen. Viewed in the simplest way, an atom of grape-sugar, for example, may be regarded as an atom of carbonic acid, in which one oxygen atom has been removed and replaced by one hydrogen atom.

"The acids so widely distributed in vegetables, such as oxalic acid (in oxalis, rumex, rheum), malic acid (in most unripe fruits), citric acid (in the lemon, lime, orange etc.), and others, stand to each other, and to carbonic acid, in a relation as simple as that between carbonic acid and grape-sugar. By the separation from a group of two carbonic acid atoms, of one oxygen atom, oxalic acid (anhydrous) is formed. If to a group of two atoms of oxalic acid two atoms of hydrogen be added, and from the whole two atoms of oxygen be removed, malic acid is the result. We have every reason to believe that by a continuance of such changes sugar, starch, and woody fibre are formed, and that they (the acids) are links in a chain exhibiting the gradual conversion of the atom of carbonic acid into sugar and the other more complex organic atoms."

Sugar can be easily converted into tartaric acid, malic acid, and oxalic acid; the inverse problem, to build up sugar from more simple molecules, is nearly solved.

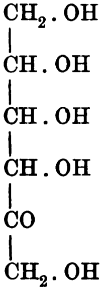
The sugars occurring in nature are divided into two classes, glucoses, $C_6H_{12}O_6$, and saccharoses, $C_{12}H_{22}O_{11}$. To the latter belongs cane-sugar, which, when heated with dilute sulphuric acid is resolved into equal molecules of two sugars belonging to the first class and called grape-sugar or dextrose and fruit-sugar or lævulose. Both contain five alcoholic hydroxyls, dextrose being at the same time an aldehyde and lævulose a ketone—

Dextrose.



$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CHO \end{array}$$

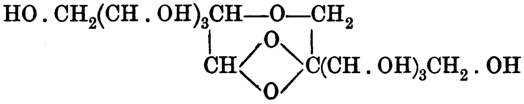
Lævulose.



$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CO \\ | \\ CH_2.OH \end{array}$$

The constitution of cane-sugar is not exactly understood; it behaves neither like a ketone nor an

aldehyde, and contains eight hydroxyls. The following constitution appears probable :—



Although we can easily resolve cane-sugar into dextrose and lævulose, we are as yet unable to obtain it again from these two glucoses; but Emil Fischer, by a series of splendid researches, has succeeded in preparing the two latter by a complete synthesis, and at the same time he has obtained a lævulose turning the plane of polarised light to the right, and a dextrose turning it to the left. In order to avoid confusion, Fischer has introduced a new nomenclature, calling the sugars with six atoms of carbon in the molecule, the *hexoses*, whilst the old name of dextrose becomes now *glucose*, and that of lævulose is changed into *fructose*.

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Loew afterwards found that by treating formaldehyde with lime-water, *formose*, $C_6H_{12}O_6$, a kind of sugar, was formed, which was probably a constituent of methylenitane, the latter being regarded as a mixture. By using magnesia instead of lime another sugar called *methose* was obtained.

In the meantime Fischer and Tafel had found that when the first product of the oxidation of glycerol, $CH_2(OH)CH(OH)CH_2(OH)$, was treated with a dilute

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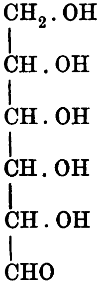
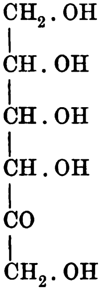


$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CHO \end{array}$$

Lævulose.



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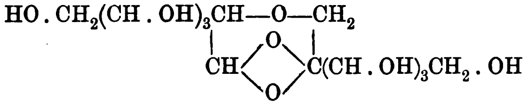

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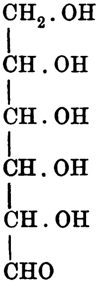
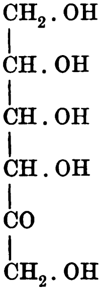


$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CHO \end{array}$$

Lævulose.



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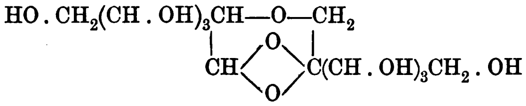

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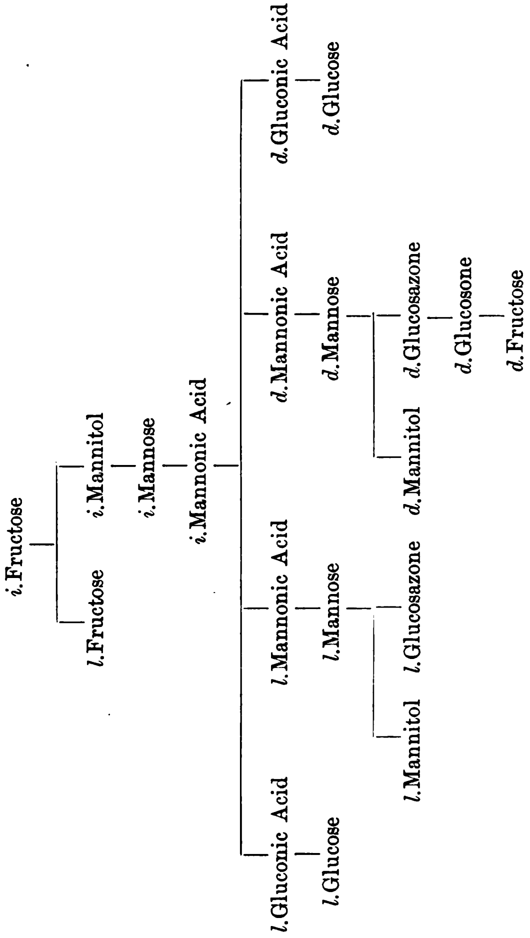
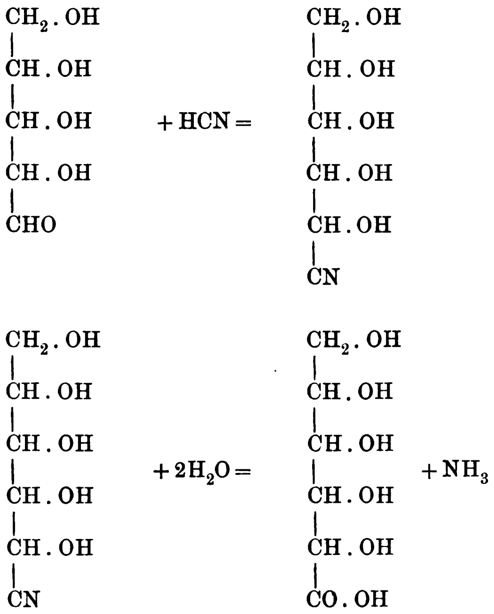

i. Fructose
l. Fructose
i. Mannitol
i. Mannose
i. Mannonic Acid
l. Gluconic Acid
l. Glucose
l. Mannonic Acid
l. Mannose
l. Mannitol
l. Glucosazone
d. Mannonic Acid
d. Mannose
d. Mannitol
d. Glucosazone
d. Glucosone
d. Fructose
d. Gluconic Acid
d. Glucose

Besides the hexoses, $C_6H_{12}O_6$, we also know sugars containing five atoms of carbon in a molecule or pentoses, such as *arabinose*, $C_5H_{10}O_5$, which has been obtained by the action of dilute acids on gum arabic and is an aldehyde like dextrose. A characteristic property of the aldehydes is that they combine with hydrocyanic acid to form cyanhydrins which, by the action of hydrochloric acid are converted into acids. Kiliani transformed arabinose by this reaction into arabinosecarboxylic acid—



$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CHO \end{array} + HCN = \begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CN \end{array}$$

$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CN \end{array} + 2H_2O = \begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CO.OH \end{array} + NH_3$$

Fischer found that this acid is identical with *l.*mannonic acid, which may be reduced to *l.*mannose. Now, by the same reaction, any *hexose* may be converted into a *heptose*, $C_7H_{14}O_7$, and from these sugars with eight or nine atoms of carbon in the molecule, *octoses*, $C_8H_{16}O_8$, and *nonoses*, $C_9H_{18}O_9$, may be readily obtained.

Fischer has already prepared a number of such sugars, and a large field has been opened for synthetical work in the sugar group. Probably some of these compounds will be found as constituents of plants, inasmuch as Fischer has shown that by combining mannoheptose with hydrogen a heptad alcohol is obtained, which is identical with *perseïtol*, $C_7H_9(OH)_7$, found in the fruit of *Laurus Persea*, and formerly believed to be an isomer of mannitol.

An account of the syntheses in the sugar group is to be found in a paper cited below.[1]

The synthesis of sugars from formaldehyde has an important bearing on the question of the assimilation of carbon dioxide by plants, and lends important support to the theory long since enunciated by Baeyer to the effect that in the green parts of plants the carbon dioxide is first reduced to formaldehyde, which then undergoes polymerisation with the formation of sugars.

Baeyer does not agree with Liebig that vegetable acids are the intermediate links between carbon dioxide and the sugars or compounds related to them; for according to this view we might expect that when the reducing power of a plant is at its maximum, *i.e.* during the action of sunlight on the green parts, an accumulation of acids would take place. This has never been observed. Plants, moreover, invariably produce sugar or other carbohydrates, whereas the

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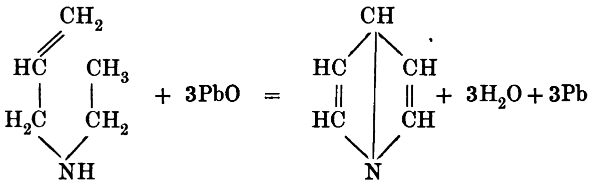
[1] E. Fischer, "Synthesen in der Zuckergruppe," *Ber. deutsch. chem. Ges.* 23, 2114.

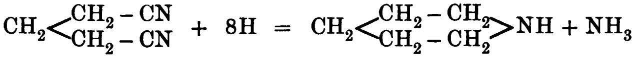
occurrence of acids varies with different species, with the age, and is generally limited to distinct parts.[1]

Plants contain poisons as well as food-stuffs, and Ladenburg by admirable perseverance has succeeded in obtaining synthetically the poison of hemlock—*conine.*

Bone-oil, obtained by the dry distillation of bones, contains a series of homologous bases, the initial members being pyridine, C_5H_5N, and picoline or methylpyridine, $C_5H_4(CH_3)N$. Pyridine has been obtained artificially by passing the vapour of ethylallylamine over heated lead oxide—



Of greater interest is its formation from piperidine, $C_5H_{11}N$, a base first observed as a product of decomposition of piperine, which is found in pepper. Ladenburg also obtained piperidine synthetically by adding sodium to a boiling alcoholic solution of trimethylene cyanide—



$$CH_2<\begin{matrix}CH_2-CN\\CH_2-CN\end{matrix} + 8H = CH_2<\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}>NH + NH_3$$

Königs found that on heating piperidine with sulphuric acid to 300° it is converted into pyridine—

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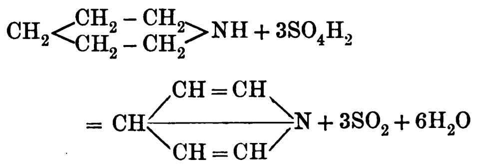
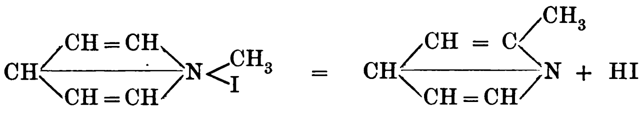
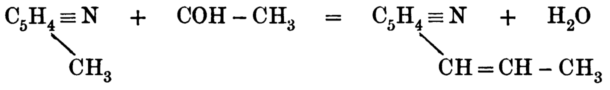
[1] *Ber. deutsch. chem. Ges.* 3, 63.



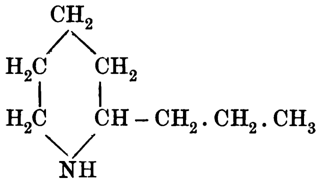
Pyridine combines with methyl iodide to form pyridine methyl-ammonium iodide, and this at 290° is converted into picoline—



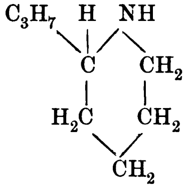
On heating picoline with paraldehyde, which under these conditions is readily converted into aldehyde, we obtain allylpyridine—

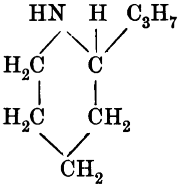


By adding sodium to a boiling alcoholic solution of the latter it combines with hydrogen and is converted into propylpiperidine having the following constitution:—



This compound differs from conine only in being optically inactive. On converting it into the tartrate, Ladenburg found that two modifications were formed; one being less soluble yielded a conine, which is perfectly identical with the natural base and is detrorotatory, whilst the more soluble tartrate gave a conine, which turns the plane of polarised light to the left. Their constitution is expressed by the formulæ—





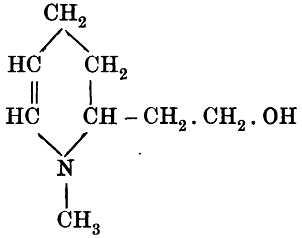
These formulæ are not identical, the sequence being in one NH, C_3H_7, H, and in the other NH, H, C_3H_7.

We may look forward also to the synthesis of nicotine, $C_{10}H_{14}N_2$, the active constituent of tobacco, which is a hexahydrodipyridyl and is converted into dipiperidyl, $C_{10}H_{20}N_2$, when sodium is added to its boiling alcoholic solution. On oxidation nicotine yields nicotinic acid, $C_5H_4N(CO_2H)$, which on heating with lime is resolved into carbon dioxide and pyridine.

Ladenburg has also ascertained the constitution of atropine, the poison of the deadly night-shade (*Atropa Belladonna*). On heating it with baryta water it is resolved into tropine, $C_8H_{15}NO$, and tropic acid, $C_9H_{10}O_3$—

$$C_{17}H_{23}NO_3 + H_2O = C_8H_{15}NO + C_9H_{10}O_3$$

Tropic acid is α - phenyl - β - oxypropionic acid, $C_6H_5 . CH(CH_2 . OH)CO_2H$, and has been obtained synthetically by several methods; whilst tropine is a methyloxyethyltetrahydropyridine, having the following constitution :—



Tropine is a powerful base and at the same time an alcohol; on combining it with tropic acid we do not get atropine again, but tropine tropate $C_8H_7ON, HO.CO.C_8H_9O$, a crystalline body which does not possess the most valuable and characteristic property of atropine, that of dilating the pupil of the eye. Now Ladenburg has found that on heating tropine tropate with hydrochloric acid it is converted into atropine which is an ethereal salt of tropic acid—

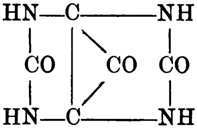
$$C_5H_7(NCH_3)C_2H_4.OH + HO.CO.C_8H_9O$$
$$= C_5H_7(NCH_3)C_2H_4O.CO.C_8H_9O + H_2O$$

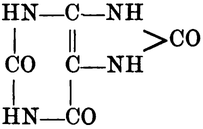
By using other acids Ladenburg has prepared a series of ethereal salts of tropine, which he calls the tropeïnes. Of these that of phenyloxyacetic acid, which is the lower homologue of phenyloxypropionic acid is the most important. Homotropeïne, $C_5H_7(NCH_3)C_2H_4O.CO.CH(OH)C_6H_5$, affects the pupil of the eye like atropine, but the action is much more rapid and the substance has therefore found a place in the materia medica.

Another alkaloid which is much employed as a local anæsthetic is found in the celebrated coca-leaves which are used as a stimulant in Bolivia and Peru in such quantities that the yearly harvest amounts to 40,000,000 lbs.[1] The leaves contain several alkaloids, of which *cocaine* is the most important. Its synthesis as well as that of atropine, will no doubt soon be an accomplished fact. The constitution of cocaine is however not yet definitely ascertained.

Uric acid, $C_5H_4N_4O_3$, which Scheele discovered in 1776 in bladder stones and called "Blasensteinsäure" (rendered into English as " lithic acid "), forms a normal constituent of the urine of mammals, birds, reptiles, different insects, etc., and has also been found in the flesh of the alligator, in the lungs, spleen, liver, and brain of the cow. Liebig and Wöhler showed, in their classical investigation, that it yields a number of most interesting derivatives. The number of these was increased by Schlieper, and Baeyer showed that most of them are compound ureas, and that uric acid itself contains three carbon atoms in direct combination and two residues of urea.

Fittig therefore proposed the first of the two following formulæ, and Medicus the second:—





The beautiful researches of E. Fischer proved that the constitution of uric acid is represented by the second formula. We can replace hydrogen in uric acid by metals and by alcohol radicals. If Fittig's formulæ were correct only one methyluric acid could

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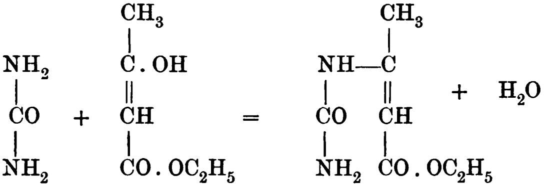
[1] *Kew Bull.* Jan. 1889.

exist; but Fischer proved that two different methyl derivatives were obtainable, one of which on oxidation gave methyl-alloxan and urea, and the other alloxan and methyl urea, and therefore the second formula had to be accepted.

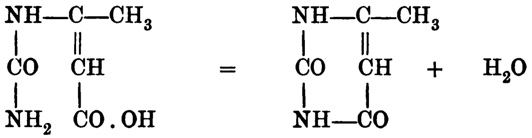
Strecker had already shown that when uric acid is heated with hydriodic acid, it is resolved into amido-acetic acid, carbon dioxide, and ammonia. As the two latter compounds are the products of decomposition of urea, Horbaczewski heated amidoacetic acid with urea, and obtained among other products a minute quantity of uric acid. A somewhat better yield was obtained by replacing the amido-acetic acid by trichlorolactamide, $CCl_3 . CH(OH)CO . NH_2$, the use of which is quite in accordance with the Medicus formula; but in this case the quantity of bye-products was again very large. The very simple synthesis discovered by Behrend and Roosen marks therefore an important advance.

They started with aceto-acetic ester, which by heating with urea yields ethyl uramidocrotonate—



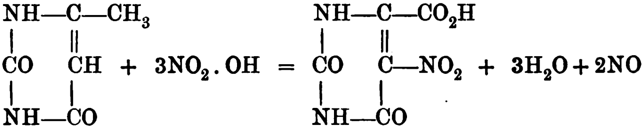
$$\begin{array}{c} NH_2 \\ | \\ CO \\ | \\ NH_2 \end{array} + \begin{array}{l} CH_3 \\ | \\ C . OH \\ \| \\ CH \\ | \\ CO . OC_2H_5 \end{array} = \begin{array}{ll} & CH_3 \\ & | \\ NH— & C \\ | & \| \\ CO & CH \\ | & | \\ NH_2 & CO . OC_2H_5 \end{array} + H_2O$$

On heating this with potash the potassium salt of uramidocrotonic acid is obtained, from which on the addition of an acid the free acid is not obtained because it at once gives off water and is converted into methyluracil—



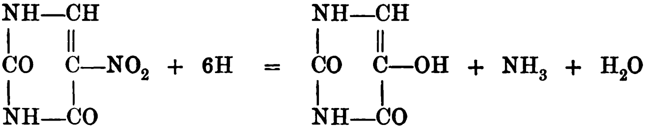
$$\begin{array}{ll}\mathrm{NH{-}} & \mathrm{C{-}CH_3}\\ | & \|\\ \mathrm{CO} & \mathrm{CH}\\ | & |\\ \mathrm{NH_2} & \mathrm{CO.OH}\end{array} \quad = \quad \begin{array}{ll}\mathrm{NH{-}} & \mathrm{C{-}CH_3}\\ | & \|\\ \mathrm{CO} & \mathrm{CH}\\ | & |\\ \mathrm{NH{-}} & \mathrm{CO}\end{array} \quad + \quad H_2O$$

If this be treated with nitric acid, we get nitro-uracilcarboxylic acid—



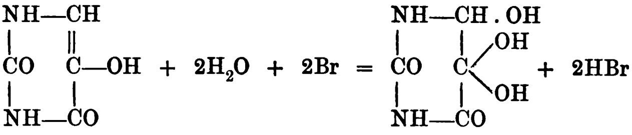
$$\begin{array}{ll}\mathrm{NH{-}} & \mathrm{C{-}CH_3}\\ | & \|\\ \mathrm{CO} & \mathrm{CH}\\ | & |\\ \mathrm{NH{-}} & \mathrm{CO}\end{array} + 3NO_2.OH = \begin{array}{ll}\mathrm{NH{-}} & \mathrm{C{-}CO_2H}\\ | & \|\\ \mathrm{CO} & \mathrm{C{-}NO_2}\\ | & |\\ \mathrm{NH{-}} & \mathrm{CO}\end{array} + 3H_2O + 2NO$$

When nitro-uracilcarboxylic acid is boiled with water it is resolved into carbon dioxide and nitro-uracil, and by treating the latter with hydrochloric acid and tin it is partly converted into amido-uracil and partly into hydroxyuracil—



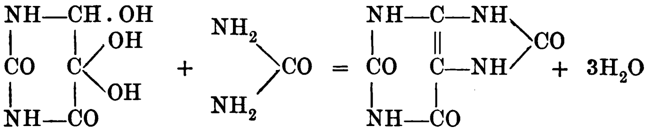
$$\begin{array}{ll}\mathrm{NH{-}} & \mathrm{CH}\\ | & \|\\ \mathrm{CO} & \mathrm{C{-}NO_2}\\ | & |\\ \mathrm{NH{-}} & \mathrm{CO}\end{array} + 6H = \begin{array}{ll}\mathrm{NH{-}} & \mathrm{CH}\\ | & \|\\ \mathrm{CO} & \mathrm{C{-}OH}\\ | & |\\ \mathrm{NH{-}} & \mathrm{CO}\end{array} + NH_3 + H_2O$$

Bromine-water oxidises hydroxyuracil, forming a compound which has been called isodialuric acid, because it is isomeric with dialuric acid or tartronylurea, which is a product of the decomposition of uric acid. Isodialuric acid is formed according to the equation—



$$\begin{array}{ll}\mathrm{NH{-}} & \mathrm{CH}\\ | & \|\\ \mathrm{CO} & \mathrm{C{-}OH}\\ | & |\\ \mathrm{NH{-}} & \mathrm{CO}\end{array} + 2H_2O + 2Br = \begin{array}{ll}\mathrm{NH{-}} & \mathrm{CH.OH}\\ | & |\\ \mathrm{CO} & \mathrm{C}\begin{array}{l}\diagup \mathrm{OH}\\ \diagdown \mathrm{OH}\end{array}\\ | & |\\ \mathrm{NH{-}} & \mathrm{CO}\end{array} + 2HBr$$

Now when this is gently heated with urea and concentrated sulphuric acid, we obtain uric acid—



Scheele observed that when uric acid was evaporated with nitric acid a red residue was obtained, which, as Prout showed, dissolved in ammonia with a purple red colour, the compound thus formed crystallising in small prisms with a metallic beetle-green lustre. The preparation of this beautiful body, which Prout called purpurate of ammonia was, however, very uncertain until Wöhler and Liebig ascertained the conditions under which it is produced. Murexide (murex, the purple-shell fish) as they called it, is a true colouring matter, and when it was found that Peruvian guano contains a large quantity of uric acid, murexide was manufactured by Mr. Rumney in Manchester, and employed in the dyeing of wool and silk. But very soon afterwards the cheaper aniline colours were discovered, and murexide was superseded.

Guano, however, can be used for the preparation of two other interesting compounds—caffeïne, $C_8H_{10}N_4O_2$, which is found in coffee, tea, and other plants, and theobromine, $C_7H_8N_4O_2$, a constituent of cacao. The constitution of these bodies, which are nearly related to uric acid, has been elucidated by E. Fischer, and no doubt their synthesis will soon be effected. They are not obtained from uric acid but from guanine, $C_5H_5N_5O$, which occurs together with uric acid in guano. Nitrous acid converts it into xanthine, $C_5H_4N_4O_2$, which is also found in small quantities in urine as well as in the flesh and other parts of the animal organisms. It forms a lead-compound, $C_5H_2PbN_4O_2$, which when heated with methyl iodide yields dimethylxanthine or theobromine, $C_5H_2(CH_3)_2N_4O_2$; by replacing one atom of hydrogen in theobromine by silver and treating the silver theobromine with methyl iodide, we get trimethylxanthine or caffeïne.

XI

The Synthesis of aromatic compounds—Benzene—Benzoic acid—Oil of bitter almonds—Salicylic acid—Cumarin—Vanillin—Colouring matters of madder-root.

A LARGE number of aromatic compounds have been obtained by synthesis; of these we will describe only such as are of more general interest. It has already been stated that all aromatic bodies are derivatives of benzene, which Berthelot first obtained synthetically. He heated acetylene, obtained by the direct union of its elements, to a dull red heat—

$$3C_2H_2 = C_6H_6$$

Since that time other synthetical methods have been found. R. Kane observed in 1837, that when acetone is heated with sulphuric acid it is converted into mesitylene, which Fittig recognised as trimethylbenzene, $C_6H_3(CH_3)_3$. On oxidation it yields trimesic acid, $C_6H_3(CO_2H)_3$, which when heated with lime is resolved into carbon dioxide and benzene—

$$C_6H_3(CO_2H)_3 = C_6H_6 + 3CO_2$$

By acting with bromine on benzene, we obtain monobromobenzene, which, as Fittig and Tollens found, is converted by the action of methyl iodide and sodium into methylbenzene or toluene—

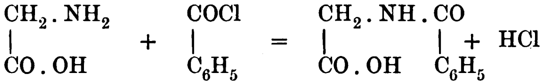
$$C_6H_5Br + CH_3I + 2Na = C_6H_5 . CH_3 + NaBr + NaI$$

In a similar way other homologues are obtained.

By passing carbon dioxide into a mixture of bromobenzene and sodium, Kekulé prepared benzoic acid which is found in gum benzoin and other resins—

$$C_6H_5Br + CO_2 + 2Na = C_6H_5 . CO_2Na + NaBr$$

The same acid is produced by the oxidation of toluene. Phosphorus pentachloride converts it into benzoyl chloride which when heated with amidoacetic acid yields hippuric acid, a normal constituent of the urine of horses, cows, and other graminivora—



$$\begin{array}{l} CH_2 . NH_2 \\ | \\ CO . OH \end{array} + \begin{array}{l} COCl \\ | \\ C_6H_5 \end{array} = \begin{array}{ll} CH_2 . NH . CO & \\ | & | \\ CO . OH & C_6H_5 \end{array} + HCl$$

The chief constituent of oil of bitter almonds is benzaldehyde, which is now produced on the large scale by passing chlorine into boiling toluene and heating the benzidene chloride thus formed with caustic soda—

$$C_6H_5 . CHCl_2 + 2NaOH = C_6H_5 . CHO + 2NaCl + H_2O$$

The essential oil of common cress and of the garden nasturtium consists, as shown by Hofmann, of phenylacetonitrile, which is obtained artificially by converting toluene into benzylchloride and heating this with potassium cyanide—

$$C_6H_5 . CH_2Cl + KCN = C_6H_5 . CH_2 . CN + KCl$$

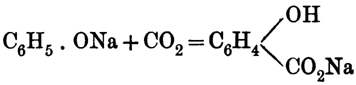
Water-cress contains the homolgous phenylpropionitrile,

$C_6H_5 . C_2H_4 . CN$, which in a similar way is obtained from ethylbenzene, $C_6H_5 . C_2H_5$.

By dissolving benzene in concentrated sulphuric acid, it is converted into benzenesulphonic acid, which when fused with caustic soda yields carbolic acid or phenol—

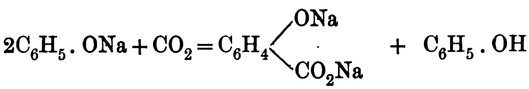
$$C_6H_5 . SO_3Na + NaOH = C_6H_5 . OH + SO_3K_2$$

Phenol is found in quantity in coal-tar, and occurs also in urine, castoreum, and the needles of the pine. It is easily transformed into salicylic or orthohydroxybenzoic acid (p. 163), which is found in different plants, its methyl ester being the chief constituent of oil of winter-green (*Gaultheria procumbens*). Kolbe and Lautemann obtained salicylic acid by passing carbon dioxide into a mixture of phenol and sodium. They explained its formation in the following manner:—



$$C_6H_5 . ONa + CO_2 = C_6H_4\begin{cases} OH \\ CO_2Na \end{cases}$$

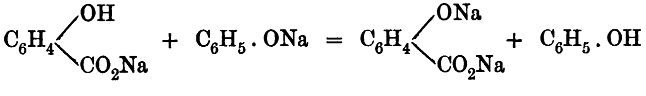
Kolbe found afterwards that it can be produced more simply by heating sodium phenate in a current of dry carbon dioxide, and he showed that the following reaction took place:—



$$2C_6H_5 . ONa + CO_2 = C_6H_4\begin{cases} ONa \\ CO_2Na \end{cases} + C_6H_5 . OH$$

R. Schmitt then proved that carbon dioxide first unites with sodium phenate to form sodium phenyl carbonate, $C_6H_5 . O . CO_2 Na$, which on heating in a closed vessel is changed into the isomeric sodium salicylate. In

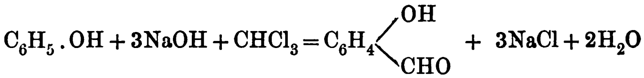
Kolbe's reaction this transformation is not complete, and at a higher temperature the sodium phenate acts on the salicylate as follows—



$$C_6H_4\Big\langle\begin{matrix}OH\\ CO_2Na\end{matrix} + C_6H_5.ONa = C_6H_4\Big\langle\begin{matrix}ONa\\ CO_2Na\end{matrix} + C_6H_5.OH$$

Salicylic acid is now manufactured by Schmitt's process; pure dry sodium phenate is placed in an autoclave, which is well cooled and a little more than the required quantity of carbon dioxide pumped into it, or it is added in the solid state. After the mixture has stood for some time, it is heated to 130°.

Salicylic aldehyde or orthohydroxybenzaldehyde is a constituent of the essential oil of the meadow-sweet (*Spiræa Ulmaria*), and other species of Spiræa; it occurs also in *Crepis fœtida*, in the larvæ of *Chrysomela populi*, living on poplars and willows, and is found in the beetles themselves. It may be obtained synthetically by the method of Reimer and Tiemann, by dissolving phenol in caustic soda and heating it with chloroform—

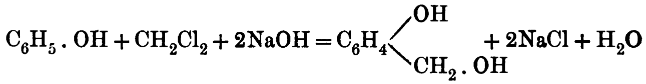


$$C_6H_5.OH + 3NaOH + CHCl_3 = C_6H_4\Big\langle\begin{matrix}OH\\ CHO\end{matrix} + 3NaCl + 2H_2O$$

The name of *glucosides* has been given to a group of compounds, which are found in the vegetable kingdom, and which by the action of certain ferments or dilute acid, are resolved in glucoses and other compounds. To these belongs salicin, found in different kinds of willow and poplar, and easily decomposed into grape-sugar and saligenin or orthohydroxybenzyl alcohol—

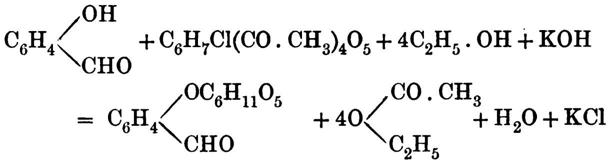
$$C_{13}H_{18}O_7 + H_2O = C_6H_{12}O_6 + C_7H_8O_2$$

The latter compound, as Greene has shown, is formed synthetically by heating phenol with methylene chloride and caustic soda—



$$C_6H_5.OH + CH_2Cl_2 + 2NaOH = C_6H_4\left\langle\begin{matrix}OH\\CH_2.OH\end{matrix}\right. + 2NaCl + H_2O$$

On oxidation saligenin yields salicylic aldehyde. Salicin on oxidation yields helicin, $C_{13}H_{16}O_7$, which on boiling with dilute sulphuric acid is decomposed into grape-sugar and salicylic aldehyde. Michael has shown that we can obtain it again from the latter compounds. If we act on grape-sugar with acetyl chloride it is converted into acetochlorhydrose, which when heated with alcoholic potash and salicylic aldehyde yields helicin—



$$C_6H_4\left\langle\begin{matrix}OH\\CHO\end{matrix}\right. + C_6H_7Cl(CO.CH_3)_4O_5 + 4C_2H_5.OH + KOH$$
$$= C_6H_4\left\langle\begin{matrix}OC_6H_{11}O_5\\CHO\end{matrix}\right. + 4O\left\langle\begin{matrix}CO.CH_3\\C_2H_5\end{matrix}\right. + H_2O + KCl$$

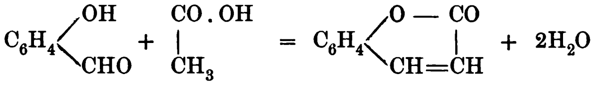
On treating helicin with water and sodium amalgam it is reduced to salicin. This is the first example of the artificial formation of a glucoside.

Several species of poplar contain populin, which on boiling with baryta-water is resolved into salicin and benzoic acid. As Schiff has found, it is also obtained by heating salicin with benzoic anhydride—

$$C_{13}H_{18}O_7 + (CO.C_6H_5)_2O = C_{13}H_{17}(CO.C_6H_5)O_7 + HO.CO.C_6H_5$$

Sweet woodruff (*Asperula odorata*) which, as Rembertus Dodonaeus, the great botanist and physician to Maximilian II., relates, is put into wine "to gladden the heart and strengthen the liver," owes its pleasant odour to Cumarin, which occurs also in the sweet vernal grass, in melilot, in the Tonka bean, and the faham-leaves (which in Réunion are used for tea), as well as in the pods of the Peru-balsam tree. Bleibtreu, who discovered it in sweet woodruff, says: "The excellent scent by which 'May-wine' is distinguished is nothing but the aroma of this stearoptene, and a purely scientific 'May-wine' prepared with cumarin was greatly enjoyed by a number of young lecturers in Bonn."

Perkin accomplished the synthesis of cumarin by heating salicylic aldehyde with sodium acetate and acetic anhydride—



$$C_6H_4\begin{array}{l}\diagup OH\\ \diagdown CHO\end{array} + \begin{array}{l}CO.OH\\ |\\ CH_3\end{array} = C_6H_4\begin{array}{l}\diagup O - CO\\ \qquad\quad |\\ \diagdown CH{=}CH\end{array} + 2H_2O$$

The synthesis of oil of cinnamon or cinnamaldehyde has already been mentioned. On oxidation it yields cinnamic acid, which is found in liquid storax, in balsam of Peru, etc. This acid is used for the preparation of artificial indigo (p. 257), and is manufactured by heating benzidene chloride with sodium acetate, a reaction discovered by Caro—

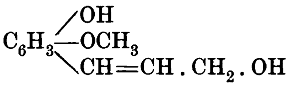
$$\begin{aligned}&C_6H_5 . CHCl_2 + CH_3 . CO_2Na\\ &\quad = C_6H_5 . CH = CH . CO_2H + HCl + NaCl\end{aligned}$$

The exquisite perfume of vanilla is due to vanillin which is now prepared on the large scale from coniferin, a crystalline compound existing in the cambium of the silver fir, spruce, larch, and other coniferæ. This, as

Haarmann and Tiemann have found, is resolved by the action of emulsin, the ferment of almonds, into grape-sugar and coniferyl alcohol—

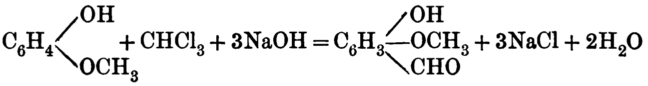
$$C_{16}H_{22}O_8 + H_2O = C_6H_{12}O_6 + C_{10}H_{12}O_3$$

Coniferyl alcohol has the following constitution:—



$$C_6H_3\begin{array}{l}\diagup OH\\ -OCH_3\\ \diagdown CH{=}CH\,.\,CH_2\,.\,OH\end{array}$$

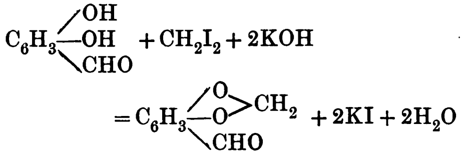
On oxidation it yields vanillin, which as Reimer and Tiemann found, can also be obtained from catechol or orthodihydroxybenzene, $C_6H_4(OH)_2$, a crystalline body, which was first observed among the products of dry distillation of catechu, and is also found in the autumnal leaves of the Virginia Creeper and other plants. The monomethyl ether of catechol has been obtained artificially by fusing phenol ortho-sulphonic acid with potash, and heating with the calculated quantity of methyl iodide and an alkali. By heating with chloroform and soda it yields vanillin—



$$C_6H_4\begin{array}{l}\diagup OH\\ \diagdown OCH_3\end{array} + CHCl_3 + 3NaOH = C_6H_3\begin{array}{l}\diagup OH\\ -OCH_3\\ \diagdown CHO\end{array} + 3NaCl + 2H_2O$$

To obtain it from the trees they are cut down, the bark removed and the cambium scraped off; the liquid portion is heated to the boiling-point, filtered and evaporated to one-fifth. On standing, coniferin crystallises out and is then oxidised with a solution of potassium dichromate in dilute sulphuric acid.

When catechol is heated with chloroform and caustic soda, it is converted into protocatechuic aldehyde, which by the action of methylene iodide and potash is converted into the methylene ether or piperonal—



$$C_6H_3{<}\begin{matrix}OH\\OH\\CHO\end{matrix} + CH_2I_2 + 2KOH$$

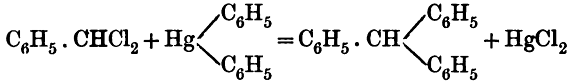
$$= C_6H_3{<}\begin{matrix}\begin{matrix}O\\O\end{matrix}{>}CH_2\\CHO\end{matrix} + 2KI + 2H_2O$$

This compound forms crystals having exactly the sweet odour of the flowers of the heliotrope, commonly called "cherry-pie," and it is therefore used in perfumery. Vanillon, a kind of fleshy vanilla, coming from the West Indies, has the same smell, and is employed for the preparation of essence of heliotrope. Haarmann and Tiemann found that it does not contain piperonal, but vanillin and another body which seems to be oil of bitter almonds, and perfumers generally add some of the latter to the alcoholic extract of vanillon. On adding benzaldehyde to an alcoholic solution of vanillin the odour of both compounds can be easily distinguished for some time, but after months the mixture acquires the smell of heliotrope.

The formation of the beautiful aniline colours depends also on a synthetical process.

The first aniline dye to be prepared on the large scale was mauve, which was obtained by Perkin in 1856, by oxidising commercial aniline with chromic acid. A magenta colour was subsequently obtained by the use of other oxidising agents.

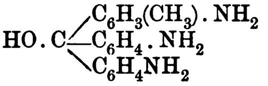
The constitution of the aniline colours was elucidated by E. and O. Fischer in 1878. They proved them to be derivatives of the hydrocarbon triphenylmethane, which was first obtained by Kekulé, by treating bromobenzene, C_6H_5Br, with sodium amalgam, and heating the mercury-phenyl so obtained with benzidene chloride—



$$C_6H_5\,.\,CHCl_2 + Hg\left\langle\begin{array}{l}C_6H_5\\C_6H_5\end{array}\right. = C_6H_5\,.\,CH\left\langle\begin{array}{l}C_6H_5\\C_6H_5\end{array}\right. + HgCl_2$$

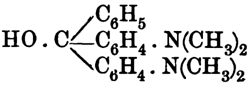
If the hydrocarbon be oxidised by chromic acid a tertiary alcohol, triphenylcarbinol, $(C_6H_5)_3C\,.\,OH$, is formed, and when hydrogen in the benzene nuclei of this is replaced by basic groups such as NH_2, $N(CH_3)_2$, $N(C_6H_5)_2$, we obtain basic substances which, though themselves colourless, give coloured salts—the so-called aniline dyes. The following are examples of the bases :—

Rosaniline base.



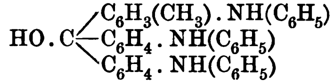
$$HO\,.\,C\left\langle\begin{array}{l}C_6H_3(CH_3)\,.\,NH_2\\C_6H_4\,.\,NH_2\\C_6H_4NH_2\end{array}\right.$$

Base of malachite green.



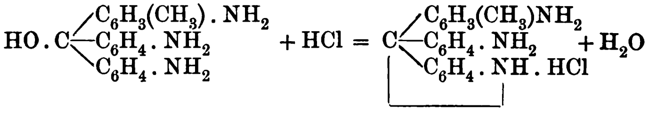
$$HO\,.\,C\left\langle\begin{array}{l}C_6H_5\\C_6H_4\,.\,N(CH_3)_2\\C_6H_4\,.\,N(CH_3)_2\end{array}\right.$$

Base of aniline blue.



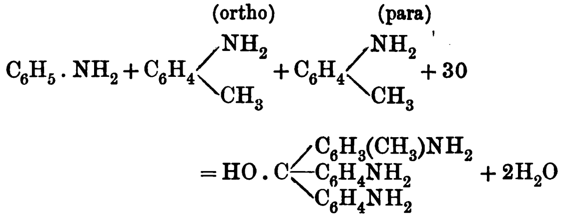
$$HO\,.\,C\left\langle\begin{array}{l}C_6H_3(CH_3)\,.\,NH(C_6H_5)\\C_6H_4\,.\,NH(C_6H_5)\\C_6H_4\,.\,NH(C_6H_5)\end{array}\right.$$

These bases combine with acids to form salts. Thus the colourless rosaniline base reacts with hydrochloric acid to form the dye magenta—



$$HO\,.\,C\left\langle\begin{array}{l}C_6H_3(CH_3)\,.\,NH_2\\C_6H_4\,.\,NH_2\\C_6H_4\,.\,NH_2\end{array}\right. + HCl = C\left\langle\begin{array}{l}C_6H_3(CH_3)NH_2\\C_6H_4\,.\,NH_2\\C_6H_4\,.\,NH\,.\,HCl\end{array}\right. + H_2O$$

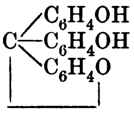
The formation of magenta from commercial aniline is explained by the fact that the latter substance when first manufactured was a mixture of three substances—aniline, ortho-toluidine, and para-toluidine. On oxidation the following reaction occurs :—



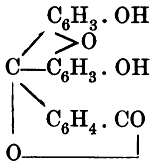
$$C_6H_5 . NH_2 + C_6H_4{<}^{NH_2}_{CH_3} + C_6H_4{<}^{NH_2}_{CH_3} + 3O = HO . C{\leqslant}\begin{matrix}C_6H_3(CH_3)NH_2\\ C_6H_4NH_2\\ C_6H_4NH_2\end{matrix} + 2H_2O$$

If hydrogen in the benzene nuclei of triphenylcarbinol is replaced by hydroxyl, phenolic substances are obtained, which combine with alkalis to form coloured salts. The following are examples :—

Aurin.



Fluorescein.



The term aniline colours comprises a great number of other classes of aromatic compounds which have been prepared artificially. The artificial dyes are now numbered by hundreds, and it is impossible here to enter into an enumeration even of the classes. We may however mention one reaction which has been of great importance in the preparation of colouring matters, and has besides considerable theoretical interest. This is the "diazo reaction" discovered in 1858 by Peter Griess. It consists in the action of nitrous acid on an amido compound, generally of the aromatic series. Thus aniline is converted into diazobenzene—

Aniline hydrochloride. Diazobenzene chloride.

$$C_6H_5 . NH_2 . HCl + HNO_2 = C_6H_5 - N = N - Cl + 2H_2O$$

Diazobenzene is a very unstable compound but readily combines with phenols and aromatic bases to form stable derivatives, the salts of which have tinctorial properties.

We might increase the number of these examples considerably. In conclusion we will give the history of the synthesis of the madder colours and indigo.

The root of madder (*Rubia tinctorum*) or other species of Rubia has been employed in India and Egypt for dyeing and calico-printing since very early times, and the methods used have undergone little change. Pliny tells us: "Pingunt et vestis in Ægypto inter pauca mirabili genere, candida vela postquam attrivere illinentes non coloribus, sed colorem sorbentibus medicamentis. Hoc cum fecere, non adparet in velis: sed in cortinam pigmenti ferventis mersa, post momentum extrahuntur picta. Mirumque, cum sit unus in cortina colos, ex illo alius atque alius fit in veste, accipientis medicamenti qualitate mutatus. Nec postea ablui potest: ita cortina non dubie confusura colores, si pictos acciperet, digerit ex uno, pingitque dum coquit. Et adustae vestes firmiores fiunt, quam si non urerentur."[1]

The cloth in which the mummies are wrapt has been dyed by this process.

The culture of madder was carried on in early times in the East and in Italy; in Holland it com-

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[1] *Nat. Hist.*, Lib. xxxv. cap. xlii.

menced in the sixteenth, and in Alsace in the seventeenth century; that of Avignon, however, was believed to be the best, and was introduced in 1762 by an Armenian, who brought the seed with him from his native country.

In the eighteenth century a property of madder-root was discovered, which called general attention to it. An account of it is given by Beckmann and by Bancroft. The latter says: "The remarkable effect of madder in giving its red colour to the bones of, but not to the soft parts of animals, with whose food it had been mixed, appears to have been observed in the sixteenth century, but it was quite forgotten until John Belchier, a surgeon, happened to dine with a calico printer in Surrey, about the year 1736, and observed that the bones of some pork which made a part of the dinner, were red; when upon expressing his surprise at the fact he was told that the hog from which it was taken had been fed on bran, after it had been employed in one of the operations of calico-printing, and had thereby imbibed the colouring matter of madder roots. Mr. Belchier afterwards ascertained, by adding some powder of madder roots to the food of dunghill fowls, that a similar redness was thereby communicated to their bones; and he gave an account of his observations and experiments to the Royal Society"[1]

Madder root contains several colouring matters; of these the most important was discovered in 1826 by Colin and Robiquet, who called it alizarin, the word being derived from *alizari*, the oriental name of madder. Littré says in his dictionary: "*Espagnol*, *alizari*, *de*

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[1] Bancroft, *Philosophy of Permanent Colours*, ii. 232; Beckmann, *History of Inventions*, ii. 111; *Phil. Trans.* Abridged, viii. 79 and 83.

l'arabe asara, qui signifie le suc extrait d'un végétal par compression." My late colleague Theodores has informed me that the word comes from *azara*, to press or squeeze.

The formula of alizarin remained doubtful for a long time, although the compound had been analysed by several distinguished chemists. E. Schunck calculated from the results of his analysis the formula $C_{14}H_{10}O_4$; he then found in 1848, that by oxidation alizarin yielded alizaric acid, and Gerhardt pointed out that this body was probably identical with phthalic acid, $C_8H_6O_4$, which Laurent had obtained by oxidising naphthalene, $C_{10}H_8$. This view was confirmed by Strecker and Wolff in 1850, who, from this fact, coupled with the results of their analysis, calculated the formula $C_{10}H_6O_3$. This was generally accepted, although in 1852 Schunck brought forward fresh proofs of the validity of his formula.

Strecker and Wolff tried to convert naphthalene into alizarin, but in vain. Other chemists afterwards succeeded in transforming this hydrocarbon into a compound having the above formula, but it was found to be quite different from alizarin, and was regarded as an isomer.

Strecker continued his research, and in 1866 came to the conclusion that alizarin had the formula $C_{14}H_8O_4$, but he did not publish the data of his analysis until the discovery of the synthesis of alizarin had been made by Gräbe and Liebermann in 1868.

Baeyer had found in 1866 that phenol, C_6H_6O, loses its oxygen, when its vapour is passed over heated zinc-dust, being converted into benzene, and that similar compounds might thus be reduced to the corresponding hydrocarbons. Gräbe and Liebermann therefore applied this reaction to alizarin, and obtained anthracene, $C_{14}H_{10}$, which Dumas and Laurent had found in coal-tar, and which had been investigated by Fritzsche and Anderson. Thus Schunck's formula seemed to be confirmed, but before Strecker had published his results Gräbe and Liebermann adopted the formula $C_{14}H_8O_4$, partly for theoretical reasons, partly from a comparison of all published analyses. They found that analyses made with the purest sublimed colouring matter gave numbers agreeing best with this formula, including the early determinations of Robiquet, who had calculated a complicated formula, because the correct atomic weight of carbon was not known at the time. That Schunck found the hydrogen a little in excess is easily accounted for, as in the old method of analysis moisture could not be entirely excluded.

But how can alizarin be converted into a hydrocarbon containing two more atoms of hydrogen in the molecule than alizarin? The explanation is not difficult; zinc-dust always contains some zinc hydroxide, and alizarin is converted into anthracene according to the equation—

$$C_{14}H_8O_4 + 5Zn + Zn(OH)_2 = C_{14}H_{10} + 6ZnO$$

As soon as Gräbe and Liebermann had proved that alizarin was a derivative of anthracene, they set to work to obtain it from this hydrocarbon.

Laurent had already found that anthracene is converted by oxidation into anthracenuse, $C_{14}H_8O_2$, which was more carefully examined by Anderson, and called by him oxanthracene. This body is exceedingly stable, and hardly acted upon by oxidising agents, which attack alizarin so readily. The latter contained two atoms of oxygen more than oxanthracene or anthraquinone (as it was called by Gräbe and Liebermann) and from its behaviour it was obvious that these were present in the form of hydroxyl. They therefore heated anthraquinone with a quantity of bromine sufficient to form dibromoanthraquinone, $C_{10}H_6Br_2O_2$, and on fusing this with potash they obtained alizarin—

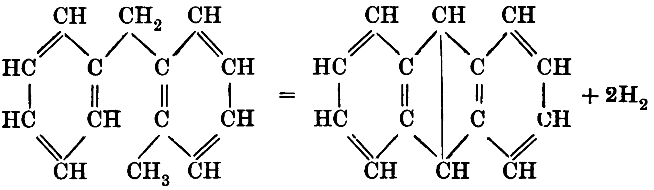
$$C_{10}H_6Br_2O_2 + 2KOH = C_{10}H_6(OH)_2O_2 + 2KBr$$

Thus for the first time a colouring matter previously produced only by plants was prepared artificially.

It was, moreover, a complete synthesis, for Limpricht had found previously that anthracene is formed when benzyl chloride is heated with water to 180°—

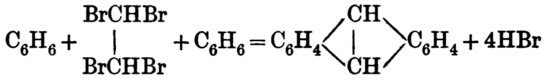
$$4C_6H_5 . CH_2Cl = C_{14}H_{10} + C_{14}H_{14} + 4HCl$$

The second hydrocarbon formed in this reaction was afterward recognised by Van Dorp as benzyltoluene, which Zincke had obtained by replacing in toluene one atom of hydrogen by benzyl. Van Dorp found that on passing its vapour through a red-hot tube, it is converted into anthracene—



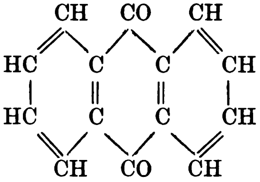
That the constitution of alizarin is represented by this formula has since been proved by other syntheses. Jackson and White obtained it by the action of sodium on orthobromobenzyl bromide, $C_6H_4Br . CH_2Br$, and

Anschütz showed that it was formed by heating a mixture of acetylene tetrabromide with benzene in the presence of aluminium bromide—

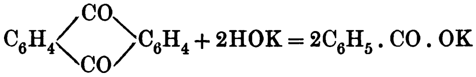


$$\mathrm{C_6H_6} + \begin{array}{c}\mathrm{BrCHBr}\\ | \\ \mathrm{BrCHBr}\end{array} + \mathrm{C_6H_6} = \mathrm{C_6H_4} \left\langle \begin{array}{c}\mathrm{CH}\\ | \\ \mathrm{CH}\end{array} \right\rangle \mathrm{C_6H_4} + 4\mathrm{HBr}$$

Anthraquinone is not only formed by oxidising anthracene, but also as Behr and Van Dorp found, by oxidising benzyltoluene to benzoylbenzoic acid, $C_6H_5 . CO . C_6H_4 . CO . OH$, and heating this with phosphorus pentoxide, which removes the elements of water. Anthraquinone has, therefore, the following constitution—

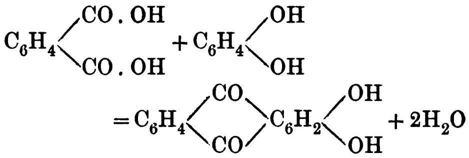


This is further proved by its being resolved into two molecules of benzoic acid, when it is fused with potash—



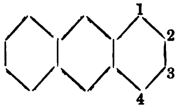
$$\mathrm{C_6H_4} \left\langle \begin{array}{c}\mathrm{CO}\\ \\ \mathrm{CO}\end{array} \right\rangle \mathrm{C_6H_4} + 2\mathrm{HOK} = 2\mathrm{C_6H_5 . CO . OK}$$

The most remarkable fact in the history of alizarin is that Gräbe and Liebermann's first attempts were successful, and that they obtained alizarin and none of its nine isomers, all of which are without value as colouring matters. It is evident that the colouring properties of alizarin are intimately connected with its constitution. Among the disubstitution products of benzene, the ortho-compounds have the most intense colour. Baeyer and Caro have shown that alizarin is an ortho-compound; they obtained it by heating orthodihydroxybenzene or catechol with phthalic acid and sulphuric acid—



$$C_6H_4\left<\begin{array}{l}CO.OH\\CO.OH\end{array}\right. + C_6H_4\left<\begin{array}{l}OH\\OH\end{array}\right.$$
$$= C_6H_4\left<\begin{array}{c}CO\\CO\end{array}\right>C_6H_2\left<\begin{array}{l}OH\\OH\end{array}\right. + 2H_2O$$

But this does not settle the question, as the following diagram shows—



According to this two ortho-compounds are possible, the hydroxyls being in the position 1 : 2 or 2 : 3. On heating phenol with phthalic acid and sulphuric acid two monohydroxyanthraquinones are formed; in one of these the hydroxyl must be in the position 1 and in the other in the position 2. Now Baeyer and Caro found that both yield alizarin when another atom of hydrogen is replaced by hydroxyl. In alizarin the hydroxyls occupy, therefore, the position 1 : 2. Baeyer and Caro arrive at the same conclusion by preparing a paradihydroxyanthraquinone from quinol, which is, therefore, called quinizarin, and in which the hydroxyls are in 1 and 4. Now on replacing in this compound or in alizarin one atom of hydrogen by hydroxyl the same trihydroxyanthraquinone is formed. This also occurs in madder, and has been called purpurin; it must contain the hydroxyls in the position 1 : 3 : 4 = 1 : 2 : 4. Madder contains also another isomer of alizarin called purpuroxanthin, which also yields purpurin by the above reaction and consequently is the 1 : 3 = 2 : 4 compound. Finally it has been found that on heating catechol with phthalic acid and sulphuric acid, the second ortho-compound is produced together with alizarin, but like the other isomers it is of no value as a colouring matter.

Gräbe and Liebermann's method for preparing alizarin cannot be used for manufacturing purposes, but, in conjunction with Caro, they devised another process, which was discovered simultaneously by Perkin. As already mentioned the conversion of benzene into phenol is effected by dissolving it in sulphuric acid, and fusing the benzene sulphonic acid thus formed with potash or soda. It was found that in the same way we may obtain alizarin by heating anthraquinone with sulphuric acid and fusing the product with soda. At the same time other hydroxyanthraquinones were produced, among them two isomers of purpurin; and one of these which was called anthrapurpurin, was found to be as valuable a dye-stuff as alizarin, yielding even more brilliant shades than the latter.

The formation of this compound could be explained by assuming that anthraquinone was converted by sulphuric acid into a disulphonic acid, $C_{14}H_6(SO_3H)_2O_2$, and a trisulphonic acid, $C_{14}H_5(SO_3H)_3O_2$, the former yielding alizarin and the latter anthrapurpurin.

It was, however, soon found that this was not the case, but that a monosulphonic and two disulphonic acids were produced, and the former only yielded alizarin, by being first converted into the 2-monohydroxyanthraquinone—

$$C_{14}H_7(SO_3Na)O_2 + 2NaOH = C_{14}H_7(ONa)O_2 + SO_3Na_2 + H_2O$$

By increasing the temperature, the monohydroxy compound is oxidised to alizarin either by the oxygen of the air, or, if this be excluded, by the soda, with accompanying evolution of hydrogen—

$$C_{14}H_7(ONa)O_2 + HONa = C_{14}H_6(ONa)_2O_2 + H_2$$

In the same way we get from the disulphonic acids two isomers of alizarin which are then oxidised to anthrapurpurin and the isomeric flavo-purpurin.

The hydrogen, which is set free, exerts a reducing action, by which a portion of the disulphonic acids may be converted into the monosulphonic acid, and this either yields alizarin or is reduced to anthraquinone again. In order to avoid this action, the mixture was heated on flat trays, thus exposing a large surface to the air; it has, however, been found that the operation proceeds best in closed vessels, some potassium chlorate being added as an oxidising agent.

When Gräbe and Liebermann published their discovery they said, "We need not point out the importance of our discovery for the madder industry if it is possible to make it a technical success. The enormous consumption of madder, the large tracts of fertile soil required for its cultivation clearly bespeak the importance which would be obtained by a new branch of industry based on the artificial preparation of alizarin from a constituent of coal-tar."

Gräbe and Liebermann's discovery produced a complete revolution in calico-printing, turkey-red dyeing, and in the manufacture of madder preparations, sooner than was expected. Madder finds to-day only a very limited application in the dyeing of wool. Twenty years ago the annual yield of madder was about 500,000 tons, of which about one-half was grown in France; ten years ago the whole export from Avignon was only 500 tons. When a friend of the author, who a few years since visited this interesting old town, asked to see the madder plantations, he was told, "it is no longer grown, as it is now made by machinery."

The discovery of artificial alizarin had not only a great influence on agriculture, but perhaps a still greater one on the industries relating to coal-tar, caustic soda, and potassium chlorate; and the manufacture of sulphur trioxide, which is used for the preparation of the sulphonic acid, has become quite a new branch of chemical industry.

Hofmann wrote in his report on the Exhibition of 1862: "England will, beyond question, at no distant day, become herself the greatest colour-producing country in the world; nay, by the strangest of revolutions, she may, ere long, send her coal-derived blues to indigo-growing India; her tar-distilled crimson to cochineal-producing Mexico, and her fossil substitutes for quercitron and safflower to China, Japan, and the other countries whence these articles are now derived."

This was just after the discovery of the aniline colours. Hofmann could then have no suspicion that Germany would be the chief seat of the colour-industry. He further quotes from a report of Menier[1] that, notwithstanding the enormous prices at which the aniline-colours were being sold, the new

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[1] *Moniteur scientifique*, 15th Sept. 1862.

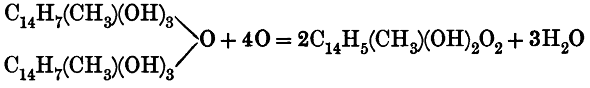
industry had already exercised a most depressing influence on the price of cochineal, of safflower, and the yellow dye-woods. Guatemala, whose chief source of revenue was cochineal, deliberated on the means of replacing it by some substitute.

To-day the same holds good for the Canaries; the progress of the colour-industry has replaced cochineal by dyes which are more easily fixed, and thus the price of oxalic acid which was much used for the dyeing of reds and yellows has also gone down considerably.

It has been mentioned that, in addition to alizarin, madder contains purpurin, which dyes shades different from those produced by the alizarin. It is now obtained from the latter by dissolving it in sulphuric acid and heating the solution with arsenic acid, one atom of hydrogen being thus replaced by hydroxyl. Purpurin, anthrapurpurin, and flavopurpurin are true colouring matters, because they contain two of their three hydroxyls in the position 1 : 2, whilst purpuroxanthin (1 : 3) does not dye, but acquires this property when an atom of hydrogen is replaced by carboxyl, so as to form purpuroxanthin carboxylic acid, $C_{14}H_5(OH)_2O_2(CO_2H)$. This body exists in common madder, and in Indian madder or munjit (*Rubia munjista*), which also contains purpurin and purpurin carboxylic acid. The latter is also found in the European madder.

Another plant which is employed in India for dyeing is A'l (*Morinda citrifolia*) which contains morindin, $C_{14}H_4(CH_3)(OH)_3O_2$. This is a derivative of methylanthracene, and so also is chrysophane or chrysophanic acid, $C_{14}H_5(CH_3)(OH)_2O_2$, which occurs in the officinal rhubarb-root and in senna, but is not a colouring matter. It is also easily obtained from chrysarobin, $C_{30}H_{26}O_7$, which forms the active constituent of Pó de Bania or Araroba powder, the medullary matter of the stem and branches of Andira Araroba. This substance has for a long time been used in Brazil for skin diseases; it was imported by the Portuguese to Goa, and hence is generally called Goa powder. Instead of using the drug, the chrysarobin is extracted from it and used in syphilitic and parasitic affections of the skin.

Liebermann has shown that its alkaline solution absorbs oxygen from the air forming chrysophanic acid—



$$\left.\begin{matrix}C_{14}H_7(CH_3)(OH)_3 \\ C_{14}H_7(CH_3)(OH)_3\end{matrix}\right\rangle O + 4O = 2C_{14}H_5(CH_3)(OH)_2O_2 + 3H_2O$$

He found that its medical action depends on this property. Now as chrysarobin is a product of reduction of chrysophanic acid, and alizarin by the action of zinc-dust and ammonia yields a body resembling chrysarobin, he concluded that the "anthrarobin" thus obtained would have a similar action. This has been fully confirmed, and anthrarobin is preferred to chrysarobin because it does not produce inflammation of the skin. The isomers of alizarin and the trihydroxyanthraquinones yield also "anthrarobins" having the same therapeutic action.[1]

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[1] *Ber. deutsch. chem. Ges.* 21, 474.

XII

Synthesis of indigo—Indigo blue—Indigo-rubin—Problems still to be solved—Conclusion.

ANOTHER brilliant discovery is the synthesis of indigo, the Indian colour, which is derived from several species of Indigofera and other plants. Indigo is mentioned by Dioscorides and Pliny. The latter says:

"Ab hoc maxima auctoritas Indigo. Ex India venit, arundinum spumae adhaerscente limo: cum teritur, nigrum: at in diluendo mixturam purpurae coeruleique mirabilem reddit. Alterum genus ejus est in purpurariis officines innatans cortinis: et est purpurae spuma. Qui adulterant, vero Indico tinguunt stercora columbina: aut cretam Selinusiam vel annulariam vitro inficiunt. Probatur carbone. Reddit enim, quod sincerum est, flammam excellentis purpurae: et dum fumat, odorem maris."

The ancients used Indigo only as a pigment, as they did not understand how to get it into solution. It was also well known to the Arabians, but in Europe it only became generally known and valued after the discovery of the sea route to India. It had been used for dyeing in very early times in India as well as in Egypt, where mummies were sometimes wrapped round with ribbon dyed by this colour. In Europe the dyeing of blue was done with woad (*Isatis tinctoria*) which also belongs to the indigo-yielding plants. It is also mentioned by Dioscorides, and Pliny informs us that it was used for dyeing wool by the Gauls, and that their wives and daughters painted their bodies with it, when they appeared naked at the sacred festivals. Cæsar relates the same of the Britons, who however did it in order to appear more terrible in battle.

In France and Germany the cultivation of woad was carried on in the sixth century; to prepare it for dyeing purposes it had to undergo a fermentation by which ammonia was evolved; the smell of this gave such offence to Queen Elizabeth, as Hume tells us in his history, that she issued an edict to prohibit the cultivation of woad.

The introduction of indigo met with violent opposition from the large vested interests of the growers of woad, and its use was interdicted in England, Germany, and France. The French king, Henry IV., even went so far as to issue an edict, condemning to death any one who used that pernicious drug called "devil's food."

The first German writers who complain of woad being banished by indigo, ascribe the fault to the Dutch. Becher says, in complaining that the manufactories were going backwards instead of progressing, "thus we give our gold to the Dutch for the trumpery colour indigo, and let the cultivation of woad in Thuringia go to perish."

However, in spite of all opposition and edicts, indigo soon superseded the native dye-stuffs.

When indigo is carefully heated, the colouring matter volatilises as a purple vapour, as Pliny mentions, and condenses in blue crystals. In this way it was first obtained in the pure state by O'Brien, who says: "The curious may sublime indigo, and thereby procure flowers as with zinc, sulphur, etc. For experiments in a small scale it may be done in a common flask over a common fire, defending the flask from the contact of the fire."[1] The pure indigo-blue or indigotin thus prepared was analysed by Walter Crum and by Laurent, who established the formula C_8H_5NO, which for theoretical reasons was afterwards changed into $C_{16}H_{10}N_2O_2$. That this is the molecular formula was afterwards proved by Sommaruga, who determined the vapour density of indigotin.

On distilling indigo with caustic soda, Fritzsche in 1840 obtained an oily base, which he called aniline, C_6H_7N, from *anil* (Arabic, the blue; Sanscrit, *nîla*, dark blue, *nīlâ*, the indigo-plant), with which name indigo was first brought to Europe by the Portuguese.[2]

By boiling indigo with caustic soda and black manganese oxide, he obtained in the next year anthranilic acid, which was subsequently found to be orthoamidobenzoic acid, $C_6H_4(NH_2)CO_2H$, and which, as Fritzsche observed, is decomposed by heat into carbon dioxide and aniline. About the same time the oxidation products of indigo were examined independently by Laurent and Erdmann.

They obtained isatin, $C_8H_5NO_2$, which forms reddish brown crystals, but is no colouring matter. Its further investigation led to very interesting discoveries such

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[1] *A Treatise on Calico Printing*, printed for C. O'Brien, Islington, 1792.

[2] My late colleague, Theodores, has informed me that the name of the Nile is of the same origin, one of its branches still being called pleonastically the Blue Nile.

as that of the substituted anilines (p. 48), but these we must leave as not bearing on our subject, and proceed to the year 1865, when Baeyer and Knop found that isatin on treatment with sodium amalgam and water is reduced to dioxindol, $C_8H_7NO_2$. This forms yellow needles and reacts again with hydrogen in an acid solution to form oxindol, C_8H_7NO, crystallising in colourless needles. On passing its vapour over red-hot zinc dust this is reduced to indol, C_8H_7N, which forms colourless crystals and which, as Nencki and Kühne found, is also a product of pancreatic digestion, and is contained in fæces, imparting to them a characteristic odour.

Baeyer and Emmerling showed, in 1869, that indol is also formed, when cinnamic acid (p. 235) is converted by means of nitric acid into orthonitrocinnamic acid, and this is heated with iron filings and potash—

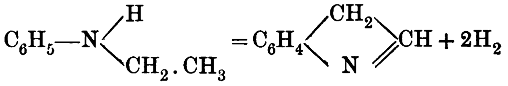
$$C_8H_6(NO_2)CO_2H = C_8H_7N + CO_2 + O_2$$

For theoretical reasons, they doubled the formula of indol, and found in the next year that on heating isatin with a mixture of phosphorus trichloride, acetylchloride, and phosphorus to 75° or 80° a green solution was obtained, which, when poured into water, deposited on standing a blue powder, consisting of indigotin and another compound which was probably isomeric, and which they called indigo-purpurin.

It has long been known that indigo-blue is sometimes deposited from urine. Jaffé found in 1870, that it is so obtained after injecting indol under the skin. Nencki confirmed this in 1875, and found also that by the action of ozonised air on indol, suspended in water, a small quantity is converted into indigo, the greater portion, however, undergoing further oxidation.

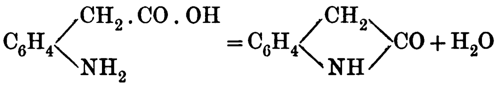
The synthesis of indigo was thus completed, but its constitution remained still in the dark, and until this had been elucidated and the molecular formulæ of the derivatives ascertained, more simple synthetical methods could not be found.

Nencki in 1876 determined the vapour density of indol, and found it in accordance with the simple formula C_8H_7N. Baeyer and Caro found, the year following, that indol is obtained by passing the vapour of ethylaniline through a red-hot tube—



$$C_6H_5{-}N\begin{matrix}\diagup H \\ \diagdown CH_2 . CH_3\end{matrix} = C_6H_4\begin{matrix}\diagup CH_2 \diagdown \\ \diagdown \; N \; \diagup\!\!\diagup\end{matrix}CH + 2H_2$$

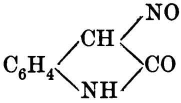
In the next year Baeyer obtained oxindol from phenyl acetic acid, $C_6H_5 . CH_2 . CO_2H$, which is readily obtained by synthesis, its nitrile being formed by heating benzyl chloride with potassium cyanide. By the action of nitric acid it is converted into orthonitrophenylacetic acid, $C_6H_4(NO_2)CH_2 . CO_2H$, which by reduction yields orthoamidophenylacetic acid, and this, like other ortho-compounds, easily loses the elements of water and forms an anhydride, which is identical with oxindol—



$$C_6H_4\begin{matrix}\diagup CH_2 . CO . OH \\ \diagdown NH_2\end{matrix} = C_6H_4\begin{matrix}\diagup CH_2 \diagdown \\ \diagdown NH \diagup\end{matrix}CO + H_2O$$

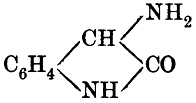
Baeyer and Knop had already shown that by the action of nitrous acid oxindol is converted into nitroso-oxindol. This may be reduced to amido-oxindol which can be oxidised to isatin. Baeyer therefore expressed the constitution of these bodies as follows :—

Nitroso-oxindol.



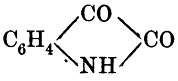
$$C_6H_4\left\langle\begin{matrix} CH\langle^{NO} \\ NH \end{matrix}\right\rangle CO$$

Amido-oxindol.



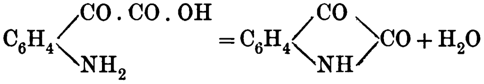
$$C_6H_4\left\langle\begin{matrix} CH\langle^{NH_2} \\ NH \end{matrix}\right\rangle CO$$

Isatin.



$$C_6H_4\left\langle\begin{matrix} CO \\ NH \end{matrix}\right\rangle CO$$

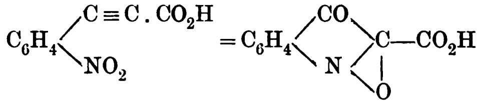
Kekulé in 1869 had already proposed this formula for isatin, and its correctness was proved by Claisen and Shadwell. By treating orthonitrobenzoic acid with phosphorus pentachloride, we obtain orthonitrobenzoyl chloride, $C_6H_4(NO_2)COCl$, which on heating with silver cyanide is converted into the nitrile, $C_6H_4(NO_2)CO . CN$, and this by the action of potash yields orthonitrophenylglyoxylic acid, $C_6H_4(NO_2)CO . CO . HO$. On reducing it the amido-acid is formed and this readily splits up into water and the anhydride which is isatin—



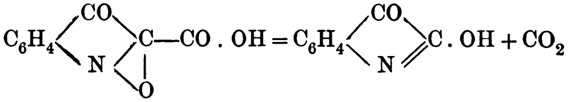
$$C_6H_4\left\langle\begin{matrix} CO . CO . OH \\ NH_2 \end{matrix}\right. = C_6H_4\left\langle\begin{matrix} CO \\ NH \end{matrix}\right\rangle CO + H_2O$$

From isatin a mixture of indigotin and indigo purpurin can be obtained. In order to clear up this reaction, Baeyer treated isatin with phosphorus chloride only, and obtained isatin chloride, C_8H_4ClNO, which by nascent hydrogen was reduced to indigotin.

To get further insight into its constitution, Baeyer returned to orthonitrocinnamic acid, $C_6H_4(NO_2)CH : CH . CO_2H$, and combined it with bromine to form nitrophenyldibromopropionic acid, $C_6H_4(NO_2)CHBr . CHBr . CO_2H$, which by the action of soda is converted into nitrophenylpropiolic acid, $C_6H_4(NO_2)C : C . CO_2H$. On warming an alkaline solution of this compound with a reducing agent, a large quantity of indigo-blue is produced, whilst by dissolving the acid in sulphuric acid it is transformed into the isomeric isatogenic acid—

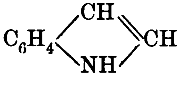


Water decomposes the latter compound into carbon dioxide and isatin, from which reaction we must deduce the following constitution for isatin—

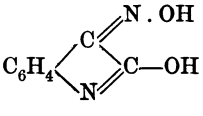


Baeyer proved this by other reactions and also that the constitution of indol and nitroso-oxindol or isatoxim is different from that given above—

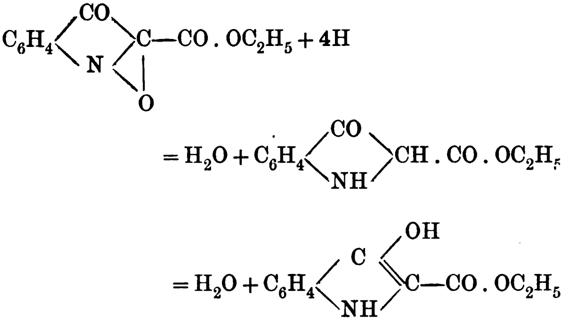
Indol.



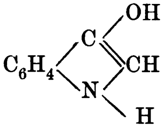
Isatoxim.



Whilst isatogenic acid is very unstable, its ethyl ester can be easily obtained by the action of sulphuric acid on ethyl nitrophenylpropiolate. Both compounds are easily reduced to ethyl indoxylate, another molecular change taking place by which the pseudo-indoxylic acid is converted into indoxylic acid—

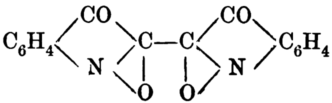


If an alkaline solution of indoxylic acid be exposed to the air, it absorbs oxygen, and indigo-blue separates out, and on boiling it with water it is resolved into carbon dioxide and indoxyl, having the constitution—



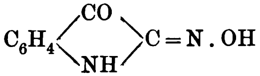
This is an oily liquid, which was first obtained from indoxylsulphuric acid. It occurs in urine and is the source of the indigo which sometimes is deposited from urine.

Baeyer proved next that in indigotin all the carbon atoms are directly combined, by obtaining it from dinitrodiphenyldiacetylene, $C_6H_4(NO_2)C\equiv C.C\equiv C.C_6H_4(NO_2)$, which by the action of sulphuric acid is converted into di-isatogene—

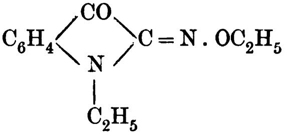


This is easily reduced to indigo-blue, and, since the latter is also readily obtained from indoxyl, it appears to contain two imido-groups. But as the compounds of this group so frequently undergo molecular changes, the existence of these groups had to be proved by experiment. A compound having the constitution which was assigned to isatin from its synthesis does not exist in the free state, but derivatives of this pseudo-isatin are known. Of these Baeyer has obtained the following—

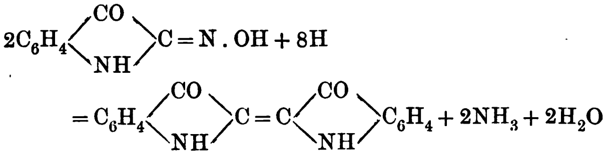
Pseudoisatoxime.

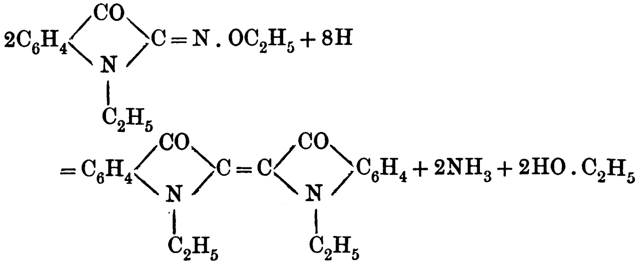


Ethylpseudoethylisatoxime.

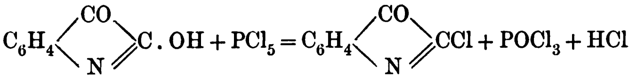


Both are easily reduced by ammonium sulphide, the former yielding indigotin, and the latter ethyl-indigotin—

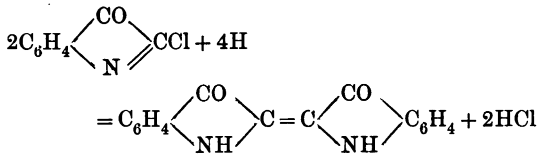




The reduction of isatin to indigo takes places by the following reactions—

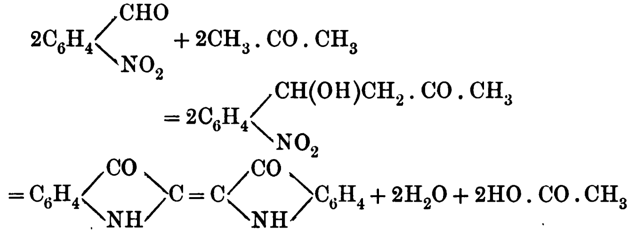


$$C_6H_4{<}\begin{matrix}CO\\N\end{matrix}{>}C.OH + PCl_5 = C_6H_4{<}\begin{matrix}CO\\N\end{matrix}{>}CCl + POCl_3 + HCl$$



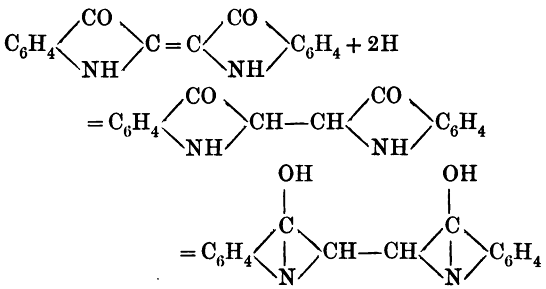
$$2C_6H_4{<}\begin{matrix}CO\\N\end{matrix}{>}CCl + 4H = C_6H_4{<}\begin{matrix}CO\\NH\end{matrix}{>}C = C{<}\begin{matrix}CO\\NH\end{matrix}{>}C_6H_4 + 2HCl$$

Indigo-blue has been obtained synthetically by other reactions. Thus it is easily obtained, as Baeyer and Drewsen found, by the action of soda on a mixture of acetone and orthonitrobenzaldehyde. These first combine to form a ketone, which decomposes into water, acetic acid, and indigotin—

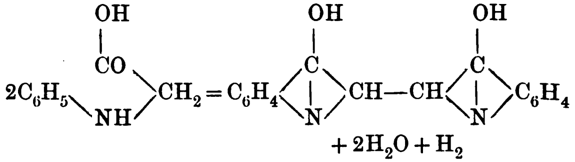


$$2C_6H_4{<}\begin{matrix}CHO\\NO_2\end{matrix} + 2CH_3.CO.CH_3 = 2C_6H_4{<}\begin{matrix}CH(OH)CH_2.CO.CH_3\\NO_2\end{matrix} = C_6H_4{<}\begin{matrix}CO\\NH\end{matrix}{>}C = C{<}\begin{matrix}CO\\NH\end{matrix}{>}C_6H_4 + 2H_2O + 2HO.CO.CH_3$$

Another very simple synthesis has been discovered by Flimm, who obtained indigo from bromacetanilide, $C_6H_5.NH.CO.CH_2Br$, which is easily obtained by the action of bromacetyl bromide, $CH_2Br.COBr$, on aniline. On heating this with caustic potash and dissolving the product in water, a solution was obtained which when exposed to the air quickly turned green and then deposited indigo. Heumann then obtained it in a similar way from phenylamidoacetic acid, $C_6H_5 . NH . CH_2 . CO . OH$; the deep yellow melt thus obtained most probably contains indigo-white, which is also formed, together with isatin, by fusing indigo-blue with caustic potash, or, more simply still, by the action of nascent hydrogen on indigo in the presence of an alkali. Indigo-white possesses the character of a phenol, and, according to Baeyer, is formed in the following way—



Now this compound can be easily produced from phenylamido-acetic acid—

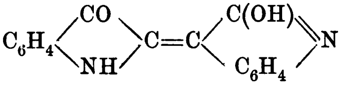


Indigo-white readily absorbs oxygen from the air and is again converted into indigo-blue.

Artificial indigo has not replaced the natural product, the latter being still the cheaper. The property of nitrophenylpropiolic acid of being easily reduced to indigo-blue has found a limited application in calico printing.

In his first attempts to reduce isatin to indigotin, Baeyer obtained, at the same time, the isomeric indigo-purpurin which, as Schunck found, is identical with indigorubin, a small but normal constituent of indigo. Schunck has traced its formation in the leaves of *Polygonum tinctorium*, which is used in China and Japan for the preparation of indigo. He cultivated it for several years, and found that the young plants do not yield a trace, and that it can only be obtained after the leaves have attained an advanced stage of development. It dyes under the same conditions as indigo-blue, but while this gives only a dull dark blue, indigorubin dyes a fine purple. Schunck, who is an authority in these matters, thinks that if it could be obtained in quantity, it would be a most valuable addition to the dye-stuffs now in use.

Indigorubin has been further examined by Baeyer, who found that it was formed by mixing hot solutions of indoxyl and isatin, and has probably the following constitution—



In his *Letters on Chemistry* Liebig, speaking of the synthesis of inorganic compounds, says: "But of all the achievements of inorganic chemistry the artificial preparation of *lapis lazuli* was the most brilliant and the most conclusive. This mineral, as presented to us by nature, is calculated powerfully to arrest our attention by its beautiful azure-blue colour, by its remaining unchanged on exposure to air or to fire, and by furnishing us with a most valuable pigment, ultramarine.

"Ultramarine was dearer than gold; it seemed impossible to form it; for analysis had sought in vain for the colouring ingredient. It was shown to be composed of silica, alumina, and soda, with sulphur and a trace of iron; and no other body had been detected in it to which its colour could be ascribed. Yet now, simply by combining in the proper proportions, as determined by analysis, silica, alumina, soda, iron, and sulphur, thousands of pounds' weight are manufactured from these ingredients; and this artificial ultramarine is even more beautiful than the natural, whilst for the price of a single ounce of the latter we may now obtain many pounds of the former.[1]

"With the production of artificial *lapis lazuli*, the formation of mineral bodies ceased to be a scientific problem to the chemist."

Liebig predicted also that a like period would come for organic chemistry. When Ettling, in 1838, found that salicin yielded on oxidation the essential oil of *Spiraea Ulmaria*, Liebig wrote to Wöhler: "This is a remarkable fact; we shall yet make sugar and quinine and uric acid."[2] In the same year Wöhler and he published their classical research on uric acid, and wrote: "The Philosophy of Chemistry will from this work draw the conclusion that the production of all organic matters in our laboratories, in so far as they do not belong any more to the organism, must be regarded not only as probable but as certain. Sugar, salicin, and morphine will be made artificially. It is

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[1] To-day several hundreds of tons are manufactured yearly, and one hundredweight of the best quality costs only £3.

[2] Liebig's and Wöhler's *Briefwechsel*, 1, 124.

true we do not yet know the methods by which this final result will be reached, because the rudiments are unknown from which they are to be developed, but we shall know them in time.

"We have not to deal with bodies whose composition rests on assumptions,—we know that with positive certainty; we know in what proportions they are combined; we know that they are products of forces of which we are cognisant."[1]

If to-day we still cannot make morphine, quinine, and similar bodies artificially, the time is near at hand. When the author, a few years ago, visited one of the largest chemical works in Germany, where some new buildings were in course of erection, and asked what they were for, he was told: "These are our future quinine works."

If we cannot make quinine, we have already found a partial substitute in antypyrine; and its introduction into therapeutics has lowered the price of quinine considerably.

Another important problem is the synthesis of the ingredients of our daily food, such as sugar, gum, and starch. These bodies are nearly related to each other, for we can convert the two latter into different kinds of sugar, and sugars again into gums. That the synthesis of sugar is imminent has already been stated.

But it is quite different with those important parts of our food which have been called the albuminous bodies. All that we know of them is their percentage composition, and that they contain the carbon atoms linked together partly as in the aliphatic compounds and partly as in the aromatic bodies. We do not know

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[1] *Ann. Chem. Pharm.* 26, 242.

their molecular weights, the most simple formula for albumin being, according to Lieberkühn, $C_{72}H_{112}N_{18}SO_{22}$, and according to Harnack, $C_{204}H_{322}N_{52}S_2O_{66}$.

Kekulé in discussing the scientific aims and achievements of chemistry, wrote: "The hypothesis of chemical valency further leads us to the supposition that also a relatively large number of single molecules may, through polyvalent atoms, combine to *net-like*, and if we may say so, *sponge-like masses* in order thus to produce those molecular groups which resist diffusion, and which, according to Graham, are called colloids. The same hypothesis leads us, in a most natural manner, to the view already pronounced by our eminent colleague, Pflüger, that such a cumulation of molecules may extend yet further, and thus build up the *formative elements* of living organisms. Of these *mass-molecules* we may perhaps further suppose that, through the constant change of position of polyvalent atoms, they will show a constant change in the connected individual molecules, so that the whole—of course with development of electricity—is in a sort of living state; particularly so as, through similar displacements, adjacent molecules may be drawn into the circle of combination and newly-formed ones expelled."[1]

The idea thus brought forward may perhaps be expressed by saying that if ever chemists should succeed in obtaining albuminous bodies artificially, it will be in the state of living protoplasm, perhaps in the form of those structureless beings which Häckel calls the Monera.

All attempts hitherto made for the purpose of producing living matter artificially have failed. The

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[1] *Nature*, 18, 210.

enigma of life can only be solved by the synthesis of an albuminous compound.

Organic chemistry advances with giants' steps. About fifty years ago only twelve hydrocarbons were known, and twelve years ago this number had increased to about 200. To-day we are acquainted with more than 400, and many of them, as well as their numerous derivatives, have been carefully studied.

What would Gmelin say to-day? When writing his *Handbook* in 1827 he requested chemists to cease their discoveries that he might finish his work.[1]

Sixteen years later Liebig also published a handbook and wrote in the preface: "In regard to completeness of the subjects treated every one will find some wish unfulfilled; at the present moment it is quite impossible to produce something complete, for even the day after the publication of a work it ceases to be complete, every day bringing a new discovery."

But in spite of the grand development of chemistry, nay, even for this reason, a survey becomes easier from day to day. The large chapters of former handbooks treating of colouring matters, bitter principles, indifferent compounds and other bodies, which could not otherwise be arranged in the system, and which Gerhardt called "corps à sérier," become shorter and shorter, and will disappear in the course of time. If to-day such bodies are discovered they may have an interest for the pharmaceutical or technical chemist, but as long as their constitution remains unknown, or at least until efforts have been made to ascertain it, and to bring the compound into some connec-

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[1] When in 1829 it was found that pyro-uric acid and cyanuric acid were identical, Wöhler wrote to Liebig: "Gmelin will say, 'Thank God, one acid less.'"

tion with a well-defined group, they have very little interest for the theoretical chemist.

We will close this short and imperfect sketch with some words of the great historian of chemistry to whom this little work was originally dedicated:—

"To none is it allowed to enjoy for long the progress of science, and the results which the future may bring to light. The alchemists of past centuries endeavoured to prepare the elixir of life, a means by which man might be kept healthy in body and mind for an unlimited space of time. We will not discuss here the question how far this might have been a benefit to the individual or not, nor whether it might have been an advantage for science if eminent men would have continued their researches for an unlimited period. The alchemists worked in vain; it is not in our power to appropriate to ourselves the experiences and results which futurity alone can bring. But in a certain sense we are indeed enabled to prolong our life backwards into the past by appropriating the experiences of those who were before us, and by becoming acquainted with their views as thoroughly as if we had been their contemporaries. The means of doing this is also an elixir of life. May the present attempt to contribute to this end be judged with indulgence." [1]

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[1] Preface to Hermann Kopp's *Die Entwicklung der Chemie in der neueren Zeit.*

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